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THE EFFECT OF GRAIN SIZE ON HARDENABILITY

By M. A. Grossmann and R. L. Stephenson

Abstract

Steels of a wide variety of compositions, and consequently of a wide range of hardenabilities, were investigated as to the effect of grain size. Each steel was caused to have different grain sizes by heating to a series of temperatures prior to quenching, and the resulting hardenability recorded. It was found that the greater the hardenability of the steel (due to its chemical composition), the more was the hardenability affected by a change in grain size.

IT has come to be recognized that the two major controlling factors in the hardenability of steel are the composition and the grain size of the austentite about to be quenched. It is true that other factors may enter, such as nucleation of fine pearlite (nodular troostite) on inclusions, and the same may conceivably obtain for undissolved carbides, but in the great majority of cases these effects are relatively unimportant compared to the effects of austenite grain size and composition.

Since the effects of grain size and composition are present simultaneously in any observed hardenability behavior, it becomes necessary in any quantitative treatment to distinguish between the two effects, and this has been taken into account by investigators. Thus Digges (1),[1] in his study of the hardenability (critical cooling-rate) of pure iron-carbon alloys, made sure that all of the alloys were at

[1]The figures appearing in parentheses refer to the references appended to this paper.

A paper presented before the Twenty-second Annual Convention of the Society held in Cleveland, October 21 to 25, 1940. Of the authors, M. A. Grossmann is director of research, and R. L. Stephenson is metallurgist at Duquesne Works, of Carnegie-Illinois Steel Corporation. Manuscript received June 14, 1940.

about the same austenite grain size when about to be quenched. Burns, Moore and Archer (2) proposed formulas for estimating the hardenability (S. A. C. rating) of steels, and the results were shown to be different for coarse-grained and fine-grained steels. Bain (3), in showing the effect of manganese on the hardenability (ideal critical size) of 0.45 per cent carbon steels depicts a band of values in which coarse-grained steels are on the high side of the range and the fine-grained steels on the low side. The above are some of the instances of simultaneous considerations of composition and grain size, but of course there have been many considerations of the effect of grain size alone, beginning with McQuaid and Ehn's (4) discovery of the greater hardenability (absence of soft spots) in coarse-grained steels. Bain and Davenport (5) studied the time required for transformation of austenite at constant temperature, for identical steels at different grain sizes.

The present work was undertaken when it was suspected that the grain size effect on hardenability might vary in some simple, regular and determinable manner with the hardenability of the steel itself (as dictated by the composition).

The test steels were four steels of different hardenabilities, whose compositions are given in Table I.

Table I
Composition of Specimens

Steel	Carbon	Manganese	Silicon	McQuaid-Ehn
A	0.43	0.71	0.19	Fine
B	0.55	0.76	0.18	Fine
C	0.79	0.62	0.21	Fine
D	0.35	1.68	0.22	Fine

These steels, in the form of approximately 9000-pound ingots, were rolled to billets, a billet from the middle of each ingot was cut lengthwise into quarter sections, and cylindrical samples cut from the center of these quarter sections (thus at "midway" positions in the billets). The test samples of steels A, B and C were 1.50-inch rounds, and those from steel D were 3.00-inch rounds (the latter on account of the greater hardenability).

After normalizing, the cylindrical samples were heated (in a manner to protect from scaling) to various temperatures from 1430 to 2100 degrees Fahr. (775 to 1150 degrees Cent.), and held at temperature for 2 hours, to establish different austenite grain sizes. In order to assure regularity in quenching, all steels were transferred

from the high heat directly to a salt bath which was held just above the upper critical temperature; after holding a short time so as to reach this temperature, the samples, which were thus still wholly austenitic and still at the grain size attained at the high temperature, were quenched in water at room temperature in a vertical quenching tower, in which a strong current of water flowed up around the samples. This gave a quite drastic quench, the quenching severity (6), (7) having been determined to be about H = 8.

The samples were then sectioned and etched to determine the depth of hardening. The latter was done by giving the samples a metallographic polish and etch, and finding the depth of hardening by observing on the microscope the position (depth) at which the structure consisted of 50 per cent martensite and 50 per cent fine pearlite (nodular troostite). The associated grain sizes were read on the fracture of each sample. The results are shown in Table II, along with the temperature employed in each case.

Table II

Steel	(1) Max. Temp. Before Quenching, Degrees Fahr.	Fracture Grain Size	(2) On 1½-Inch Round, Depth of Hardening, Inch	(3) D_1	(4) D_1^2
A	1530	6½	0.18	0.895	0.80
	1700	5¼	0.215	1.00	1.00
	1800	4¾	0.23	1.04	1.08
	1850	3½	0.28	1.16	1.35
	2000	1½	0.35	1.30	1.69
B	1600	6¼	0.205	0.97	0.94
	1850	5	0.225	1.025	1.05
	1900	2¾	0.345	1.29	1.66
	2100	½	0.53	1.555	2.42
C	1430	6¼	0.175	0.88	0.78
	1500	5	0.205	0.97	0.94
	1600	4¾	0.215	1.00	1.00
	1900	3¾	0.265	1.125	1.27
	2000	1½	0.333	1.27	1.61
			Depth of Hardening on 3-Inch Round		
D	1525	7½	0.30	1.47	2.16
	1700	6½	0.342	1.57	2.46
	1900	5	0.393	1.72	2.96
	2000	2¼	0.58	2.20	4.84
	2100	1½	0.645	2.33	5.43

The data show different depths of hardening for the different steels, and of course a range of depths of hardening for each steel as influenced by the grain size. A question arises as to how best to show these relationships, that is to say (in plotting grain size against hardenability) what criterion to chart as the hardenability. A useful criterion is the "ideal critical size," which is defined (6) as the diameter of bar which will just "harden throughout" (absence of

unhardened core) in an ideal quench (severest possible quench). In stating that a bar "just hardens throughout" it should be pointed out that this refers to its appearance in a fracture test or an etch test, thus using the same criterion as the common one for "depth of hardening." In this case therefore, while the outer portion of the bar would be fully hardened to 100 per cent martensite, this would shade off to just 50 per cent martensite (balance fine pearlite) at the center of the bar. The depths of hardening in the table may therefore be calculated to the ideal critical size since the quenching severity is known, and the values are shown in the third column, which is marked D_I in the table. By way of illustration of such calculation, steel A, when at 6½ grain size, hardened to a depth of 0.18 inch in a 1.50-inch round, under the particular quenching conditions, where the severity of quench was $H = 8$. It can be shown (6), (7) (readily verifiable by experiment) that if a 1.50-inch diameter bar hardens to a depth of 0.18 inch, the size of bar which would just harden all the way through would be 0.78-inch diameter, this being the critical size (for this steel and at this grain size) under these quenching conditions $H = 8$. Had the quench been ideal (severest possible), the critical size, instead of 0.78 inch, would have been about 0.895 inch, which is thus the "ideal critical size," D_I. In the same way there was calculated, for each depth of hardening shown, the corresponding ideal critical size, which is the criterion of hardenability.

Instead of plotting grain size against the value D_I (which might with propriety be done), it has proven advantageous to plot the grain size against the square of D_I (i.e., D_I^2). This has the advantage of representing a pertinent metallurgical behavior in that it represents cooling time; or, more precisely, it is directly proportional to the "characteristic cooling time." This point possibly requires some explanation, which is offered in the appended Explanatory Note. Briefly, the characteristic cooling time is the time occupied in cooling which results in half-hardening (50 per cent martensite). This time varies with the hardenability of the steel, and is characteristic of it.

As mentioned, therefore, the data of Table II are plotted as grain size against hardenability in terms of D_I^2, the values of D_I^2 being shown in the column so marked in Table II. The result for these four steels is shown in the solid lines in Fig. 1. These lines indicate clearly that with increase in the hardenability of the steel (as dictated by the composition), there is an increase in the effect of the grain size on the hardenability, as represented by the characteristic

cooling time (or D_I^2). This relationship is indicated by the relative slopes of the lines.

In view of this behavior, it was of interest to ascertain whether any data in the literature accorded with the data developed here.

Table III
Compositions (Approximate)

Steel	Carbon	Manganese
1	0.40	0.80
2	0.42	0.90
3	0.75	0.30
4	0.90	0.30

Steel	Grain Size	D_I	D_I^2
1	7½	0.63	0.397
	5	0.85	0.723
	2	1.00	1.00
2	4½	0.96	0.922
	2	1.15	1.322
3	5	0.87	0.757
	4½	1.00	1.00
	4	1.06	1.122
	3½	1.11	1.232
	3	1.16	1.346
	2	1.25	1.56
4	6¼	0.85	0.723
	5	1.00	1.00
	4	1.15	1.322
	3½	1.24	1.54

Data had in the meantime been published by Bain (8) showing hardenabilities (as ideal critical size) in relation to grain size for four steels. The data are given in Table III, as read from his diagram

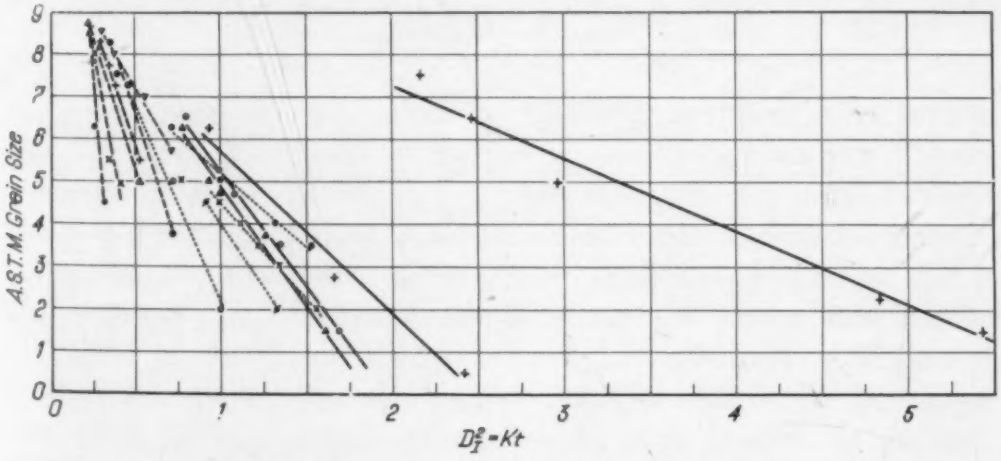

Fig. 1—Relation Between Grain Size and Hardenability. Hardenability is Stated in Terms of D_I^2, Which is Directly Proportional to the Cooling Time.

and calculated to D_I^2. These values are plotted as the dotted lines in Fig. 1. It will be seen that, again plotting the most reasonable straight lines, the behaviors accord closely with those of the steels of the low hardenabilities in the present series, and continue the trend

to somewhat lower hardenabilities. Data on tool steels furthermore were presented by Shepherd (9), giving the grain size and stating the hardenability as depth of hardening on ¾-inch rounds, when treated at a series of temperatures and quenched in a carefully described manner in brine. Since the steels were of still lower hardenability than the two groups described above, they were of special interest as showing whether the indicated trend was continued to steels of such low hardenability. In order to calculate the ideal

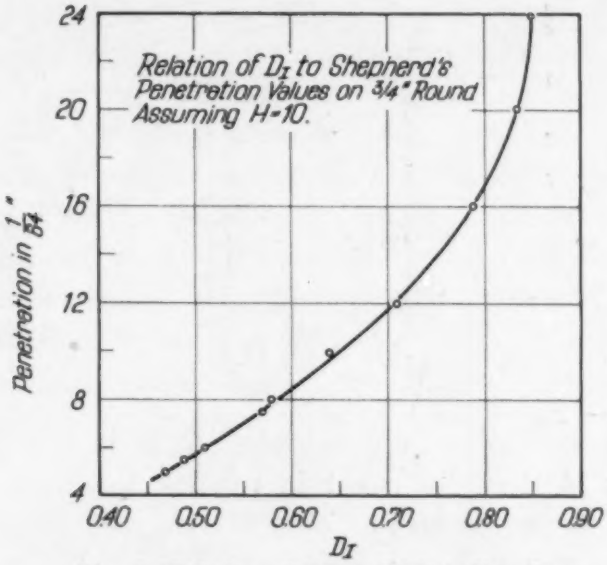

Fig. 2—Relation of Ideal Critical Size D1 to Shepherd's Penetration Values on ¾-Inch Round, Assuming Severity of Quench H = 10.

critical sizes from the depths of hardening, the probable severity of quench was estimated, and experience has shown that the strongly agitated brine quench which Shepherd described results usually in a severity of quench about H = 10. (A slight departure from this value, such as H = 8 to H = 15, would make very little difference at such high values of H). From the numerous steels described, six steels, the compositions of four of which are given in Table IV, were selected because of their wide range of as-heat-treated grain sizes and accompanying range in depths of hardening. For convenience in translating from depth of hardening to ideal critical size, the curve of Fig. 2 was drawn up, which holds for ¾-inch rounds at H = 10. The results thus deduced from Shepherd's data are given in Table V and plotted as the dashed lines in Fig. 1, and it will be seen that the trend previously recorded is continued very strikingly to the steels of low hardenability.

It may very properly be objected that inasmuch as Shepherd's steels are high in carbon, for the most part hypereutectoid, the carbides may not all have been dissolved at his lowest heat treating temperature, and that the slope of the corresponding lines shown in Fig. 1 is therefore incorrect. This is perfectly possible, but if so then the

Table IV

Steel	C	Mn	P	S	Si	Ni	Cr
6101	1.07	0.20	0.013	0.013	0.20	0.025	0.01
1D091	1.01	0.27	0.015	0.021	0.15	.....	....
5D330	1.06	0.27	0.015	0.020	0.15	.....	....
H5183	1.05	0.25	0.011	0.017	0.17	0.08	0.02

correct lines would be even steeper than those drawn in Fig. 1, so that the change in slope with change in hardenability (due to composition) would be still more pronounced than that shown, and instead of invalidating the present trend would exaggerate it. However, the very uniform way in which Shepherd's data accord with the behavior

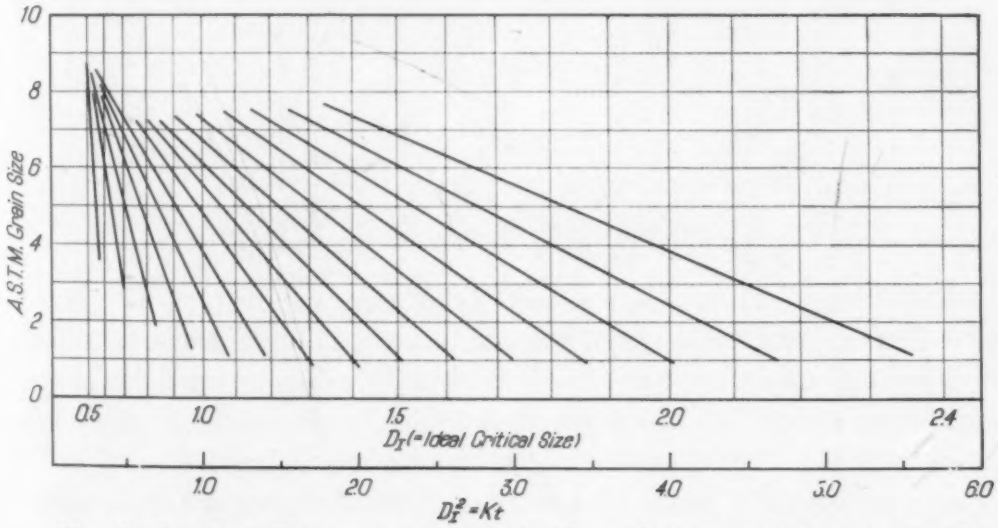

Fig. 3—Chart for Relation Between Grain Size and Hardenability, as D_1 or D_1^2, Based on Fig. 1.

of the other steels makes it seem likely that the departure, if present at all, is only slight.

It is rather striking that the data assembled from such widely different sources result in lines (on the diagram) which not only indicate a regular trend but even in some cases practically coincide. This makes it seem highly probable that if any two (or more) steels have equal hardenability at one grain size they will also have equal hardenability at some other grain size, and that it is therefore per-

missible to draw a generalized diagram. This has been done in Fig. 3, based empirically on the behaviors shown in Fig. 1, the abscissae in Fig. 3 being shown (for convenience in use) as D_I, the auxiliary scale showing D_I^2 as before.

As indicated previously, a question might arise as to the true shape of the curves in Figs. 1 and 3, which in the absence of any sufficiently precise indications to the contrary have been drawn as

Table V

Steel	Fracture Grain Size	Hardness Penetration in 64ths	D_I	D_I^2
6101	9	5	0.47	0.22
	8½	5½	0.49	0.24
	6¼	6	0.51	0.26
	4½	7½	0.57	0.325
1D091	8¼	8	0.59	0.35
	7¼	11	0.68	0.46
	3¾	24	0.85	0.72
5D330	8¼	7	0.55	0.30
	7¾	8	0.59	0.35
	7¼	9	0.62	0.38
	5½	13	0.73	0.53
H5183	8¾	5	0.47	0.22
	8½	5½	0.49	0.24
	8¼	7	0.55	0.30
	5	13	0.73	0.53
2D45	8½	7½	0.57	0.325
	8	9	0.62	0.38
	7	14	0.75	0.56
	5¾	24	0.85	0.72
5877-S	8½	5½	0.49	0.24
	8	6	0.51	0.26
	5½	8	0.59	0.35
	4¼	10	0.65	0.42

straight lines. Mehl (10) provides an analysis of rate of pearlite growth from austenite, at constant sub-critical temperature. Because of its relationship to the growth of pearlite during quenching (the present problem), it was of interest to calculate his data to the present co-ordinates. Fig. 4 shows the results when using his data for *a* (grain radius), N (rate of nucleation), G (rate of growth) and t (time), together with some extrapolations provided by Austin (11), adopting a value $N = 1.0 \times 10^6$, and $G = 1.0 \times 10^{-3}$, which are approximately the values shown by Mehl for a "eutectoid steel" at about 1080 degrees Fahr. (580 degrees Cent.). To show steels of lower and higher hardenability, G was assigned twice the above value (lower hardenability) and half the above value (greater hardenability), while N was assumed to be the same. Fig. 4 is plotted as A. S. T. M. grain size against time for production of 50 per cent pearlite (i. e. half-hardening in the present scheme), and it is quite striking that, although the slopes do not accord exactly with those

shown in Fig. 3, which was indeed scarcely to be expected, nevertheless there is an obvious similarity. It remains for further experimental work to determine whether the lines of Fig. 3 should be slightly curved, i.e., whether the behavior in quenching is in this respect analogous to the behavior at constant temperature.

There is however a still further complication in attempting to

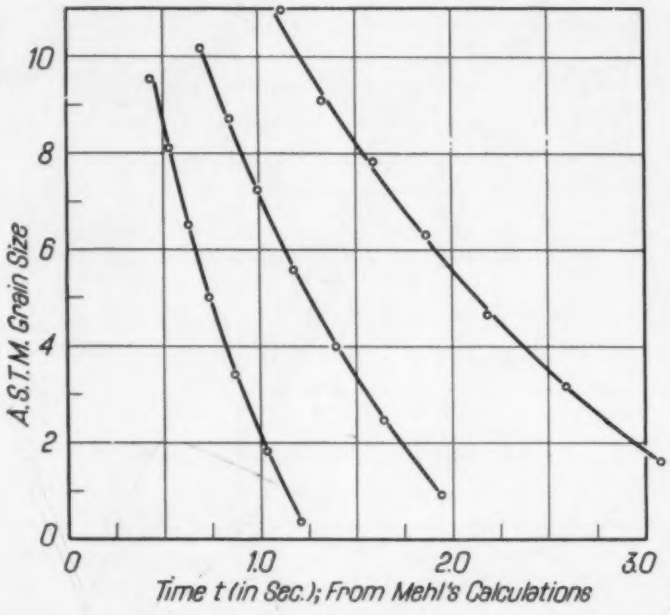

Fig. 4—Relation Between Grain Size and Time at Constant Temperature for 50 Per Cent Pearlite, Based on Mehl's Calculations.

derive the theoretically correct shape of curve, in that the grain sizes shown in Figs. 1 and 3 are fracture grain sizes, whereas the true grain sizes are undoubtedly mixtures fluctuating somewhat about the average. This would introduce further complexity. On the whole, however, it seems justifiable to conclude that Fig. 3 furnishes a guide which is quite reliable.

In view of the increasing effect of grain size as the "composition hardenability" increases, it was of interest to see whether a regular relationship would appear when plotting on semi-logarithmic coordinates. The points of Fig. 1 are therefore plotted on the semi-log scales of Fig. 5, again drawing the most reasonable straight lines. It is seen that most of the steels fall into a series of reasonably parallel straight lines, although the relationships are not by any means perfectly regular. However, the chart seems useful in suggesting rough approximations, in ranges not yet explored experimentally.

An important inference from the present work is that it again emphasizes the impossibility of evaluating the effect of chemical elements on hardenability at other than *identical grain sizes as quenched*. If two steels are to be compared when their as-quenched

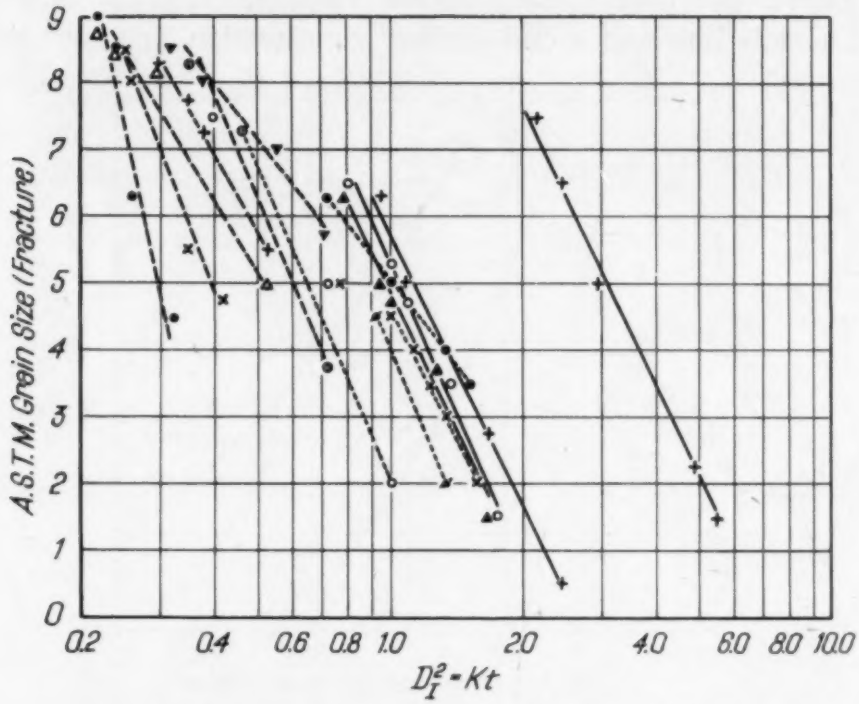

Fig. 5—Relation Between Grain Size and Hardenability (as D_I^2) on Semi-logarithmic Scales. Data Same as Fig. 1.

grain sizes differ, Fig. 3 may be employed to judge the hardenabilities at identical grain sizes. It will be seen that this precaution is particularly important for steels of the higher hardenabilities, where the hardenability of the piece being quenched is changed markedly by a change in grain size.

Explanatory Note

Possibly the meaning of the term "characteristic cooling time" will become clear when considered in relation to the term (at present more widely used and understood)—the "critical cooling rate." The critical cooling rate for any steel is the cooling rate which must be attained in quenching if the steel is to be fully hardened (100 per cent martensite). Any slower cooling rate results in the formation of at least a small amount of fine pearlite (nodular troostite) so that the steel is incompletely hardened. In contrast with the critical cooling

rate, the characteristic cooling time for any steel is defined as the time occupied in cooling (during the quench) which results in the steel being just half-hardened (50 per cent martensite, balance fine pearlite). Justification should be offered for advocating a different concept when "critical cooling rate" is already well established. Such justification is found in two points: 1. *Time instead of rate.* It was found (6) that cooling time accorded more closely with experimental values than did cooling rate, when the cooling time was the

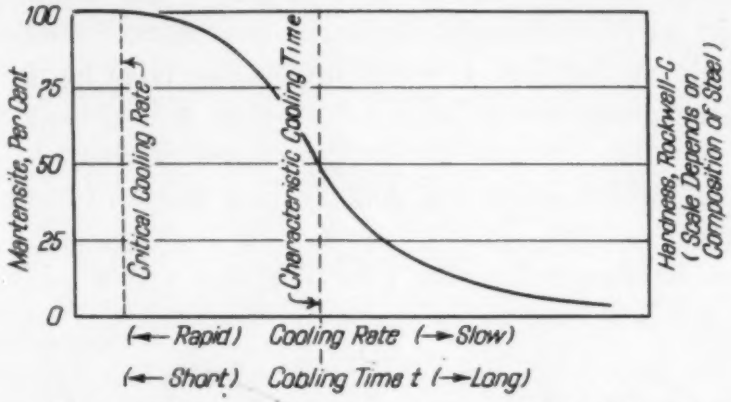

Fig. 6—Illustration of Relation Between Critical Cooling Rate and Characteristic Cooling Time.

"half-temperature cooling time" (the time to cool from the quenching temperature to a temperature halfway down to that of the quenching liquid) and the cooling rate was the rate of cooling between 1100 and 900 degrees Fahr. (595 and 480 degrees Cent.). 2. *Half-hardened instead of fully hardened.* Steels in quenching exhibit in general the behavior shown in Fig. 6. Therefore it becomes rather laborious in actual tests to determine the point at which a steel is just fully hardened, whereas it is relatively easy (because of the rapid change in proportion of martensite) to determine the point at which the steel is half-hardened (50 per cent martensite). This is illustrated in the familiar fracture or etch test for "depth of hardening,"—it is easy to read the thickness of hardened rim because at the inside of the rim the structure changes very rapidly in the neighborhood of 50 per cent martensite. At this position there is an abrupt drop in hardness, a sharp change in the fracture appearance and a marked change in etching characteristics. By contrast it is relatively difficult to determine the position at which the steel is just fully hardened to 100 per cent martensite, for it requires either careful microscopic examination or exceedingly careful hardness exploration, since (as shown

in Fig. 6) the departure from full hardening is only very gradual. The usefulness of the 50 per cent point in practice is attested by its use during the many years in which "depth of hardening" has been employed as a criterion of hardenability.

It is thus possibly clear that, just as the critical cooling rate indicates the hardenability of a steel because it is the rate at which that steel must be cooled in order to harden fully, so the characteristic cooling time is likewise an index of hardenability because it is the time which the steel occupies in cooling (to half-temperature) when it becomes just half-hardened. Now the determination of the actual characteristic cooling time (for example in seconds) by time-temperature measurements would be as laborious in this respect as the determination of the critical cooling rate, but fortunately the ideal critical size (which is readily found) is a simple function of the cooling time.

It can be shown that the time t at the center of the ideally quenched bar is related to the diameter of that bar (namely D_I) in a simple way represented by the relationship $D_I = k\sqrt{t}$, where k is a constant involving diffusivity. Therefore $D_I^2 = Kt$, meaning that time t is directly proportional to the square of the ideal critical size. Since this time t is the time at the center of the bar, where a structure of 50 per cent martensite was produced, we have a value which represents "characteristic cooling time" but states it in terms of ideal critical size. The reality of this relationship (time vs. ideal critical size) may be visualized by thinking of the bar as it would actually cool in an ideal quench. The outside cools instantly, and the inside would therefore occupy a certain length of time in cooling which would be determined by the size of the bar. Since the center of the bar, in the ideal critical size, is just half-hardened (50 per cent martensite) it is perhaps clear that the time for different steels to form 50 per cent martensite at the center of the bar is related to the bar size and in this sense represents the hardenability. Actually, as mentioned, the time at the center is proportional to the square of the bar diameter (i.e., D_I^2).

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DISCUSSION

Written Discussion: By Arthur E. Focke, research metallurgist, Diamond Chain and Manufacturing Co., Indianapolis, Ind.

To the writer, the principal value of this paper is that it again demonstrates the possibility of correlating the results of three different laboratories, on several types of steels, using various methods of quenching in order to arrive at a generalized conclusion.

However, from the standpoint of attempting to apply the results of this paper, I question the statement made by the authors on page 7 that "this makes it seem highly probable that if any two (or more) steels have equal hardenability at one grain size, they will have equal hardenability at some other grain size". The data of Fig. 1 and the generalized diagram, Fig. 3, show that if the grain size used for comparison is larger than A.S.T.M. No. 7 the statement is correct but if the comparisons were made at the finer sizes, for example at A.S.T.M. No. 8-1/2-9, it would appear to be possible to have a two to almost threefold variation in hardenability as measured by the DI^2 term when the grain size is coarsened.

Also, while the authors have been perfectly justified in choosing from the many examples in the paper by B. F. Shepherd on "The P-F Characteristics of Steels" (TRANSACTIONS, American Society for Metals, Vol. 22, p. 979), the six steels which showed a wide range of as-heat-treated grain sizes and accompanying range in depth of hardening, it is interesting that in Table II on page 987 of this article another steel designated CPX is listed which showed a twofold variation in depth of hardening with only an increase of ¼ number in fracture grain size.

This steel had a chemical analysis of:

C 0.80	P 0.023	Si 0.15
Mn 0.31	S 0.017	

Using the charts of this paper under discussion the following would result:

Temperature Degrees Fahr.	Fracture Grain Size	Hardness Penetration	DI	DI^2
1450	4½	12	0.71	0.50
1500	4½	16	0.79	0.62
1550	4½	16	0.79	0.62
1600	4¼	24	0.85	0.72

If these results are plotted on Fig. 1, it is obvious that the slope of the line through these points would be much less than those of the other steels on this chart which had similar hardenability. Obviously this steel is unusual in that it developed a coarse grain size at a very low temperature but this result would indicate that under certain circumstances steels might be obtained with grain size hardenability relationship which are not in accord with the regular trend.

These minor criticisms do not affect my opinion that this is a very interesting paper and another important contribution to our understanding of hardenability by Dr. Grossmann and his associates.

Written Discussion: By O. V. Greene and C. B. Post, The Carpenter Steel Company, Reading, Pa.

We have followed with interest the hardenability work of Dr. Grossmann and his associates for a number of years, and in general their method of analysis has been a distinct contribution to the growing literature on this subject.

In attempting to correlate many of the so-called standard hardenability tests in vogue at the present time, one is confronted first of all with the choice between the concept of critical cooling rate and the so-called critical bar diameter of Grossmann which can be stated in terms of an "ideal" critical bar diameter. In considering this latter method of analysis Dr. Grossmann has rendered a distinct service in recognizing the role of the quenching media and has enabled us to state the hardenability in terms of this ideal critical size which is independent of any quenching media, providing the severity of quench is known.

There is a distinct possibility that in the future, instead of Grossmann's method of analysis leading us to a clarification of hardenability values, it may merely change the disagreements from one concerning hardenabilities to one concerning severities of quench. This is to say, at the present time the large number of hardenability tests in use leaves only a small possibility of correlation between any two of these tests, and moreover in actual practice disagreement sometimes occurs between two laboratories concerning the hardenability as indicated by any one of these tests. Therefore it would be no less confusing to have disagreements on severity of quench than to have disagreements as at present on the methods of hardenability evaluation.

In considering the severity of quench obtained for shallow hardening steels in brine quenching media, we believe that Messrs. Grossmann and Stephenson are over-estimating the severity of the ordinary brine quench represented by the immersion of the sample in a vertical 3-inch diameter flush with about a 1-inch overflow, or the rapid agitation in brine when the specimen is held with pointed tongs.

Several experiments have been performed by our laboratory on quenching various size rounds of shallow hardening steels in both the 3-inch pipe flush and by rapid agitation of the specimens held with tongs in brine. The severity of quench obtained from these experiments, when estimated by the recommended procedure of Grossmann, et al., shows that the appropriate severity of quench amounts to H-values ranging between 4 and 5. Several experiments were conducted by outside concerns, using still-brine quenching media, to determine what range of H-values can be expected for these brine quenches, and in all cases to date, it is believed than an average number of

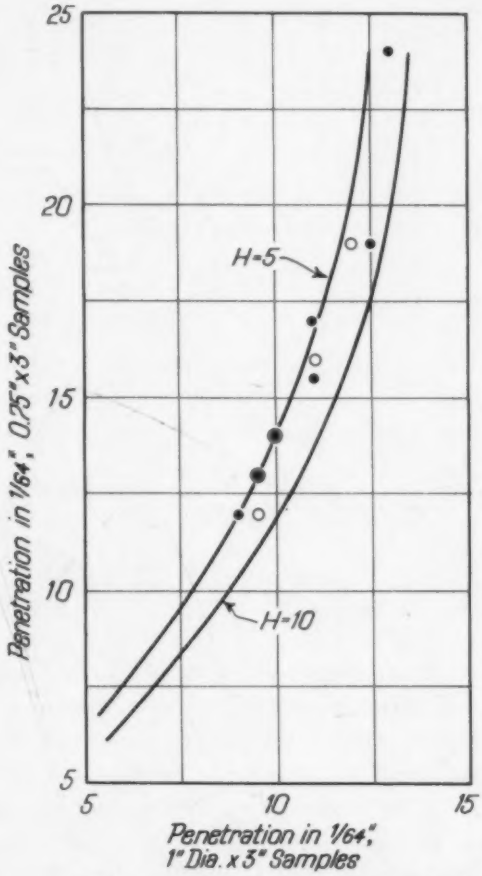


Fig. 1—Curve Showing Correlation Between Penetration in 64ths of an Inch as Measured on 1-Inch Rounds and ¾-Inch Rounds.

H = 5 would be a first approximation. This discussion is not to be confused with the H-values obtained for disks when they are quenched in a special flushing fixture as described by B. F. Shepherd.[1]

Fig. 1 of this discussion shows the correlation between penetration in 64ths of an inch as measured on 1-inch rounds and ¾-inch rounds by The Carpenter Steel Laboratories and by an independent laboratory. In Fig. 1 it may be

[1]B. F. Shepherd, "Inherent Hardenability Characteristics of Tool Steel", TRANSACTIONS, American Society for Steel Treating, Vol. XVII, 1930, p. 90.

clearly seen that a severity of quench as represented by H = 5 more nearly reproduces the experimental results than the line characteristic of H = 10. These specimens from which the results shown in Fig. 1 were obtained were quenched in the 3-inch round flush which Messrs. Grossmann and Stephenson stated "results usually in a severity of quench of about H = 10".

On the basis of these results, the assumed value of H = 10 as applied to authors' Fig. 2 is somewhat in doubt. Fig. 2 of this discussion shows experimental data obtained from ¾-inch rounds which were oil treated 1600 degrees Fahr.— 40 minutes at temperature, and then brine-quenched at temperatures

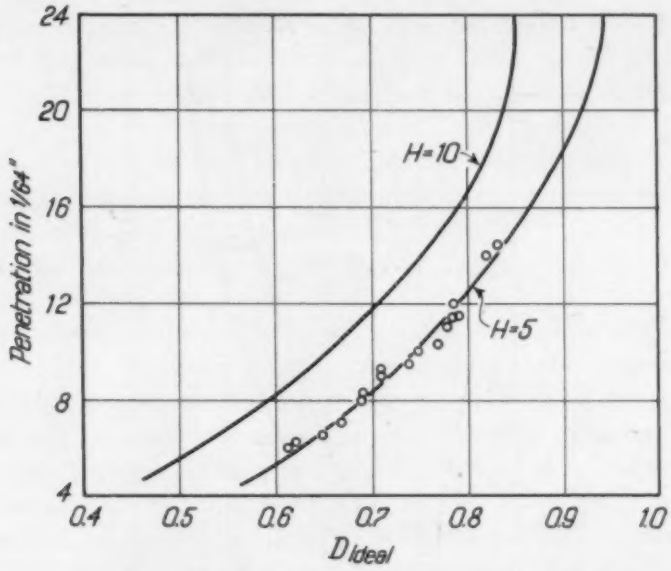


Fig. 2—Relation on Dideal To Penetration Values on ¾-Inch Round, H = 5.

ranging from 1450 to 1600 degrees Fahr. in the 3-inch vertical pipe flush mentioned above. The ideal critical diameters shown in Fig. 2 of this discussion were computed from the measured penetrations using a severity of quench of H = 5. As is to be expected, the curve representing our experimental data, which is based upon a severity of quench of H = 5, lies below the values obtained by Messrs. Grossmann and Stephenson using their assumed value of H = 10. Incidentally, the results of Fig. 2 illustrate the statement made above in regard to the possibility of confusion between laboratories concerning their severities of quench.

Referring now to the authors' Fig. 5, it is of interest to note that their experimental results all form a set of parallel linear lines. Three of the four sets of data attributed to Dr. Bain also form a set of parallel linear lines. To our minds this is indicative of a general relationship extending from the deep hardening steels down to the shallow hardening steels. In order to check this relationship we have taken P-F data from our metallurgical inspection records and plotted them on logarithmic scales similar to the method of plotting shown in authors' Fig. 5. In eight heats analyzed by this method we found only one to deviate markedly from this family of parallel linear lines.

Table I

Heat No.	Temperature Degrees Fahr.	Penetration in 64ths on ¼-Inch Round	Fracture No.	D_{Ideal} (Computed H = 5)	D_{Ideal} (Estimated From Fig. A)	Penetration (Computed)
A	1450	7	8½	0.67	....	....
	1500	8	8¼	0.69	0.685	8.0
	1550	9	6¼	0.71	0.81	12.5
	1600	....	...	....	....	....
B	1450	6	8¾	0.62	....	....
	1500	7	8½	0.67	0.63	5.5
	1550	9	7¼	0.71	0.71	9.0
	1600	12	6½	0.79	0.76	10.5
C	1450	10.5	8¾	0.77	....	....
	1500	11.5	7¾	0.79	0.85	14.5
	1550	14.0	7	0.82	0.905	18.0
	1600	...	...	....	....	....
D	1450	8	8½	0.69	....	....
	1500	9.5	8	0.74	0.714	8.0
	1550	11.5	7½	0.79	0.75	9.5
	1600	....	...	....	....	....
E	1450	9	8¾	0.71	....	....
	1500	11	7¾	0.78	0.77	10.5
	1550	14.5	6¾	0.83	0.84	15.0
	1600	....	...	....	....	....
F	1450	6	8¾	0.62	....	....
	1500	6.5	8½	0.65	0.63	5.5
	1550	8	8	0.69	0.66	6.5
	1600	10	7¾	0.75	0.68	7.5

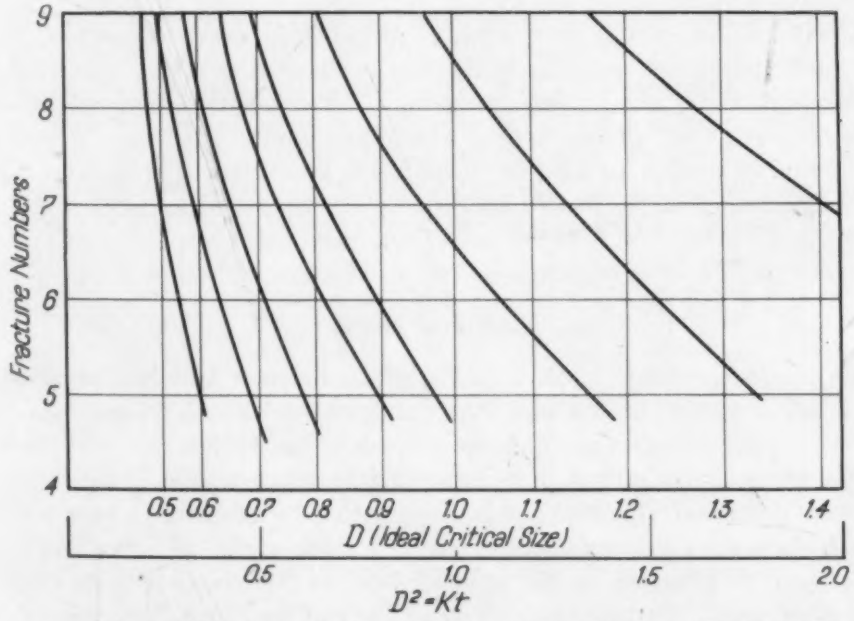


Fig. 3—Chart for Relation Between Grain Size and Hardenability, Based on Grossmann's and Carpenter Steel Company's Experimental Data.

The reason for this discrepancy is not known. Apparently this establishes the fact that the generalized family of lines in Fig. 5 are linear straight lines throughout the hardenability range, as far as we have investigated.

This general relationship was used to derive Fig. 3 of this discussion which shows the correlation between grain size and hardenability based upon the experimental results of Messrs. Grossmann and Stephenson, Bain and The Carpenter Steel Company. It is of interest to note that the lines shown in Fig. 3 are slightly curved, which is in accord with the theoretical prediction shown in authors' Fig. 4.

In order to estimate the error between experimental and computed penetrations obtained from the fracture numbers of a series of ¾-inch rounds, quenched from temperatures ranging from 1450 to 1600 degrees Fahr., Table I shows P-F tests for six different heats of 1.10 per cent carbon shallow hardening steels. The experimental penetrations on the ¾-inch rounds are shown in column 3, while the actual fracture numbers of the cases are shown in column 4. The 5th column shows the ideal critical bar diameters computed from the penetration data, using Grossmann's method of analysis and a severity of quench of $H = 5$. The 6th column shows the ideal critical bar diameter estimated from the fracture numbers (see Fig. 3) and the penetration data at 1450 degrees Fahr. The agreement is about what one would expect using these highly theoretical conversion methods. The 7th column shows the predicted penetration obtained from the estimated ideal critical bar diameter. The severity of quench was assumed here also to be $H = 5$. An analysis of the data shown in Table I leads in many cases to the conclusion that slight variations between the computed and estimated ideal critical bar diameters result in significant errors between the experimental and computed penetrations.

A word of caution at this point is probably in order concerning the use of Grossmann's charts in calculating Rockwell contours and penetrations on small rounds of shallow hardening steels. The difficulties involved in reading the charts, etc., can lead to errors which are greater than the experimental errors found in actual observation. One must appreciate that in working with shallow hardening steels these small variations of case have a definite meaning, and a difference of 1/64 or 2/64 inch may mean the difference between the success or failure of a part made from this type of steel.

Authors' Reply

We appreciate very much Dr. Focke's comments and he has done very well to call attention to the fact that the linear relationships obtained in this paper do not always obtain. This we believe is due to the fact that nucleation does not always, although it does usually, take place at the grain boundaries. That was illustrated also by data just presented by Messrs. Greene and Post, in which they showed a number of steels, I think eight. They all conformed to the linear relationship or the parallel line on the semi-log scales with the exception of one. We believe the reason for the occasional discrepancy is the fact that in occasional steels nucleation takes place within grains instead of at the grain boundaries and this method of analysis would therefore not apply. This was pointed out by Mehl in his discussion of sub-critical transformation.

With regard to the discussion by Messrs. Greene and Post, on the severity of quench, that is indeed a controversial subject about which a great deal

could be said. The analysis made by Mr. Asimow on the heat flow in bars being quenched was necessarily based on the assumption of Newton's Law of cooling. That is, the cooling is in proportion to the temperature difference between the bar and the quenching medium. The same assumption was made by Russell, in a British investigation made about the same time for the British Iron and Steel Institute.

This Newton's Law of cooling, as is known from numerous experimental data, such as Scott's data and French's data, does not apply precisely, due particularly to the vapor film, and the temperature of this vapor phase formation varies with different quenching mediums. It is for this reason, the reason of departure from Newton's Law of cooling, that the very careful experimental data presented by Messrs. Greene and Post are so welcome and we hope they will continue their work.

With regard to the difference in quenching severity between $H = 5$ and $H = 10$, it may be pointed out that in the shallow hardening steels, discussed by Messrs. Greene and Post, the sizes are small, the ideal critical sizes calculated are small and in that range, as they pointed out, there may be a significant difference between $H = 5$ and $H = 10$, because of the shape of the curves at small sizes. With larger sizes, the difference between $H = 5$ and $H = 10$ is relatively small, however.

It was very pleasant and comforting to have the confirmation of the parallel lines on the semi-log scale, and we assuredly agree with the statement that this indicates that the grain size effect is proportional to the effect of the hardenability. In other words, the greater the hardenability due to composition of the steel, the greater the effect of the grain size on the hardenability.

We believe that Messrs. Greene and Post are quite correct in showing the curved lines in their Fig. C rather than showing them straight, as we showed them in one of our diagrams, and it is very interesting to see this correspond with the isothermal transformations as deduced from Mehl's work.

We should like to express appreciation for the discussions.

STRUCTURAL CHANGES IN LOW CARBON STEELS PRODUCED BY HOT AND COLD ROLLING

By N. P. Goss

Abstract

A new method for the study of orientation textures has been developed, based on surface diffraction. It is very effective in showing variations in the orientation textures of hot- and cold-rolled strip steel, and also in the determination of the crystallographic directions predominating in the surface, rolling, and transverse rolling directions. The relative intensities of each orientation can be estimated.

Complex orientation textures cannot be adequately determined by the Laue method, but when supplemented by surface diffraction, variations in preferred orientation textures can be detected.

WHEN low carbon strip steel is hot-rolled between A_1 and A_3 preferred orientation of the fragmented grains or crystallites occurs. When the hot rolling is performed above A_3 directional properties are not as a rule developed because of the allotropic transformation which occurs when the strip is cooled through A_3. Hot-rolled strip intended for deep drawing purposes is hot-rolled in this manner.

When the surface of the hot-rolled strip is the chief consideration the hot rolling is performed below A_3, the finishing temperature usually being about 1450 degrees Fahr. The intensity of the directional properties developed depends upon the extent to which the low carbon strip steel is rolled below A_3. In practice the finishing passes are usually carried out below A_3 and the directional properties are not strongly developed unless the total reduction in thickness is rather large.

In this experiment the hot rolling was purposely performed in such a way that the greater part of the rolling was carried out below A_3 to develop a strong fiber structure.

The fiber structure of the hot- and cold-rolled strip steels was studied by X-ray diffraction methods. The objects of these experi-

A paper presented before the Twenty-second Annual Convention of the Society held in Cleveland, October 21 to 25, 1940. The author, N. P. Goss, is physicist, Cold Metal Process Co., Youngstown, Ohio. Manuscript received June 1, 1940.

ments were to determine the (a) crystallographic directions which lie in the rolling direction, in the transverse rolling direction and in a direction normal to the surface after drastic hot rolling below A_3 but above A_1, (b) the effect of subsequent cold rolling upon this hot-rolled texture, (c) to determine the possible difference in the fiber structure and describe the orientations present, (d) finally the effect of heat treatment above and below A_3 upon the directional properties of the cold-rolled strip was determined.

Preparation of Specimens

Hot Rolling—A slab of low carbon (0.105 carbon) open-hearth steel, 9⅝ inch by 2⅜ inch by 22 feet, and weighing 1700 pounds was hot-rolled on a single stand reversing hot mill to a strip 0.113 inch thick and 9 13/16 inches wide in 8 passes. The slabs were heated to 1800 degrees Fahr. (980 degrees Cent.) and rolled at a speed of 800 feet per minute; the temperature after the third pass was below A_3. The rolling schedule is given in the following table.

Pass	Inches	Per Cent Reduction
1	2.375 to 1.523	36
2	" 0.973	36
3	" 0.598	38½
4	" 0.378	33½
5	" 0.273	31½
6	" 0.193	29½
7	" 0.148	23½
8	" 0.113	23½

Cold Rolling—The hot-rolled strip was not annealed before cold rolling, but cold-rolled directly to gage according to the following schedule:

Pass	Gage Inches	Reduction in Per Cent
1	0.113 to 0.0865	23.5
2	0.0735	15
3	0.0624	15
4	0.053	15
5	0.045	15
6	0.038	15
7	0.033	15
8	0.028	15
9	0.0235	15
10	0.020	15
11	0.017	15
12	0.0144	15

Small reductions per pass had to be made because the edges of the hot strip were checked rather deeply, otherwise the strip would have fractured. The Rockwell hardness after cold rolling was B-94.

Microstructure of the Hot- and Cold-Rolled Strip

The microstructure of the hot-rolled strip is shown in Fig. 1a. The grains are elongated in the direction of rolling and the pearlite stringers appear along the grain boundaries. This shows that hot rolling below A_3 but above A_1 elongates the grains in a manner similar to cold rolling.

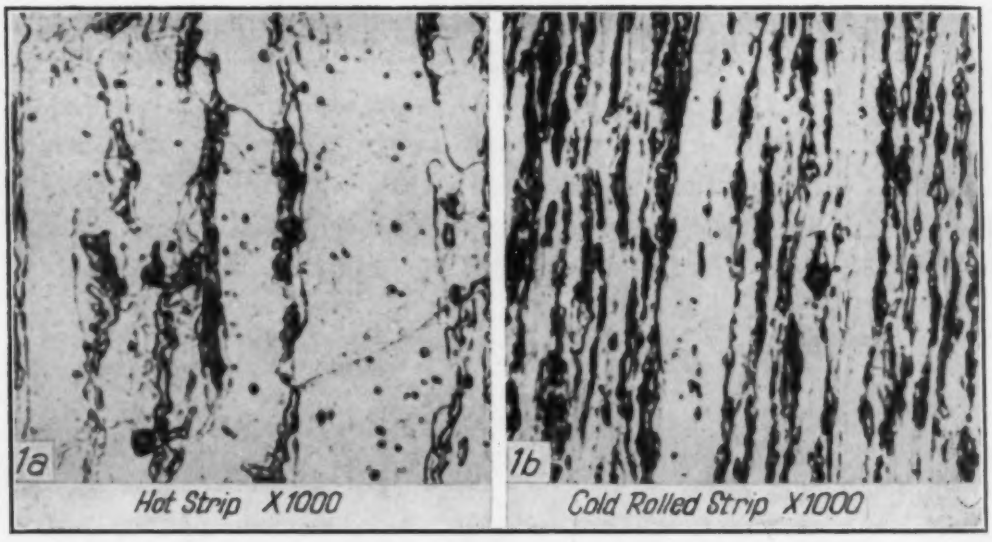


Fig. 1a—Microstructure of the Hot-Rolled Strip.
Fig. 1b—Microstructure of the Hot Strip after Cold Rolling.

Hot rolling was discontinued when the strip temperature was near 1350 degrees Fahr. (735 degrees Cent.). The microstructure does not indicate recovery nor recrystallization of the structure, but this can be determined with the X-ray.

Hot rolling under these conditions work hardens the strip to such an extent that severe edge checking occurs, due to the hardness which was Rockwell B-83. Hot-rolled strip with severely checked edges is difficult to cold roll; there is always the danger of a crack starting in an edge crack which will cause the strip to fracture during the cold rolling operation.

The microstructure of the hot strip after cold rolling is shown in Fig. 1b. The grains are also elongated in the direction of rolling. Comparing the hot-rolled and cold-rolled structures it is apparent

that hot working appears to be less drastic in so far as the intensity of fibering of the grain structure is concerned. However, the microstructure does not show the intensity of the orientation structure of the crystallites which is developed by hot or cold rolling. Actually the elongated grains consist of many small fragments oriented definitely in the direction of rolling. To determine the true fiber structure in the hot- and cold-rolled strip X-ray diffraction methods must be used.

Method of X-Ray Examination

It was found by experiment (a) that the Laue method by itself cannot adequately determine the orientation textures and must be supplemented by X-ray surface diffraction diagrams. This is especially true when several orientation textures are present and in varying proportions. Also when several orientations appear to be present the problem is further complicated in that one is confronted with the problem of differentiating between true grain orientations and those due to zonal planes. To simplify this problem, emphasis was not placed on crystal orientation but rather to determine the crystallographic directions which lie in the rolling direction, transverse rolling direction, and in the surface of the strip. By following this method it is possible to see whether the same crystallographic directions are present in the hot- and cold-rolled strip and whether they are present in the same strength. The Laue and surface diffraction method was used in attacking this problem.

The source of X-rays was a water-cooled Coolidge tube with a molybdenum target. The tube was operated at 35,000 volts and 12 milliamperes. The pin hole and slit systems used in the Laue and surface diffraction cassettes defined a beam of small divergence thus assuring sharp diffraction lines which is a prime requisite in all branches of diffraction work. The surface diffraction required an exposure of only 260 milliampere hours while some of the Laue patterns required exposures up to 2500 milliampere hours. These long exposures were necessary to bring out weak diffraction maxima in the lines of higher order and indices.

The Laue X-ray diffraction patterns were made by transmitting the X-ray beam through thin sections cut parallel to the surface, rolling, and transverse rolling directions. The X-ray diagrams made of the specimens cut in this way will be referred to as "N", "T", and

"P" diagrams. This method was described in a previous paper in detail (1a).[1]

The surface diffraction diagrams were made by reflecting the X-ray beam from the surface, the edge parallel to the rolling direction, and the edge parallel to the transverse rolling direction. These will be referred to as "N", "T", and "P" surface diffraction diagrams respectively. The angles of incidence were chosen in the following way. If a certain crystal plane lies in the surface of these specimens it will diffract the X-ray beam strongly when the Bragg condition is fulfilled ($N \lambda = 2 d \sin \Theta$). Table I shows the angles the X-ray beam must make with the surface in order to diffract the X-ray beam from important crystal planes for α iron—provided they are present in the surface of these specimens. If there are a great many atom planes in the surface a strong one will be present on the X-ray film when the specimen is set at the required angle. A line of weak intensity will be formed on the X-ray film when only a small number of atom planes lie in the surface.

Table I

Crystal Plane (α iron)	Angle of Incidence For Mo. Kα Radiation
(110)	10° 6′
(100)	14° 22′
(211)	17° 35′
(111)	25° 30′
(123)	28°

These hot- and cold-rolled strip steels were therefore studied by two methods of X-ray analysis, the conventional Laue method and the surface diffraction method developed by the author. By combining these two methods the most complicated orientation textures can be easily determined. From a practical point of view it is usually the difference in orientation textures which is the more important rather than a knowledge of the exact orientation present. This point is emphasized here and the results will bear out this viewpoint.

Examination of X-ray Diffraction Diagrams

The Laue Diagrams—The Laue diagrams of the hot- and cold-rolled strip steels will be considered first. These are shown in Fig. 2. They have been arranged so that corresponding diffraction diagrams made in the "P", "T", and "N" directions are directly compared.

[1]The figures appearing in parentheses refer to the bibliography appended to this paper.

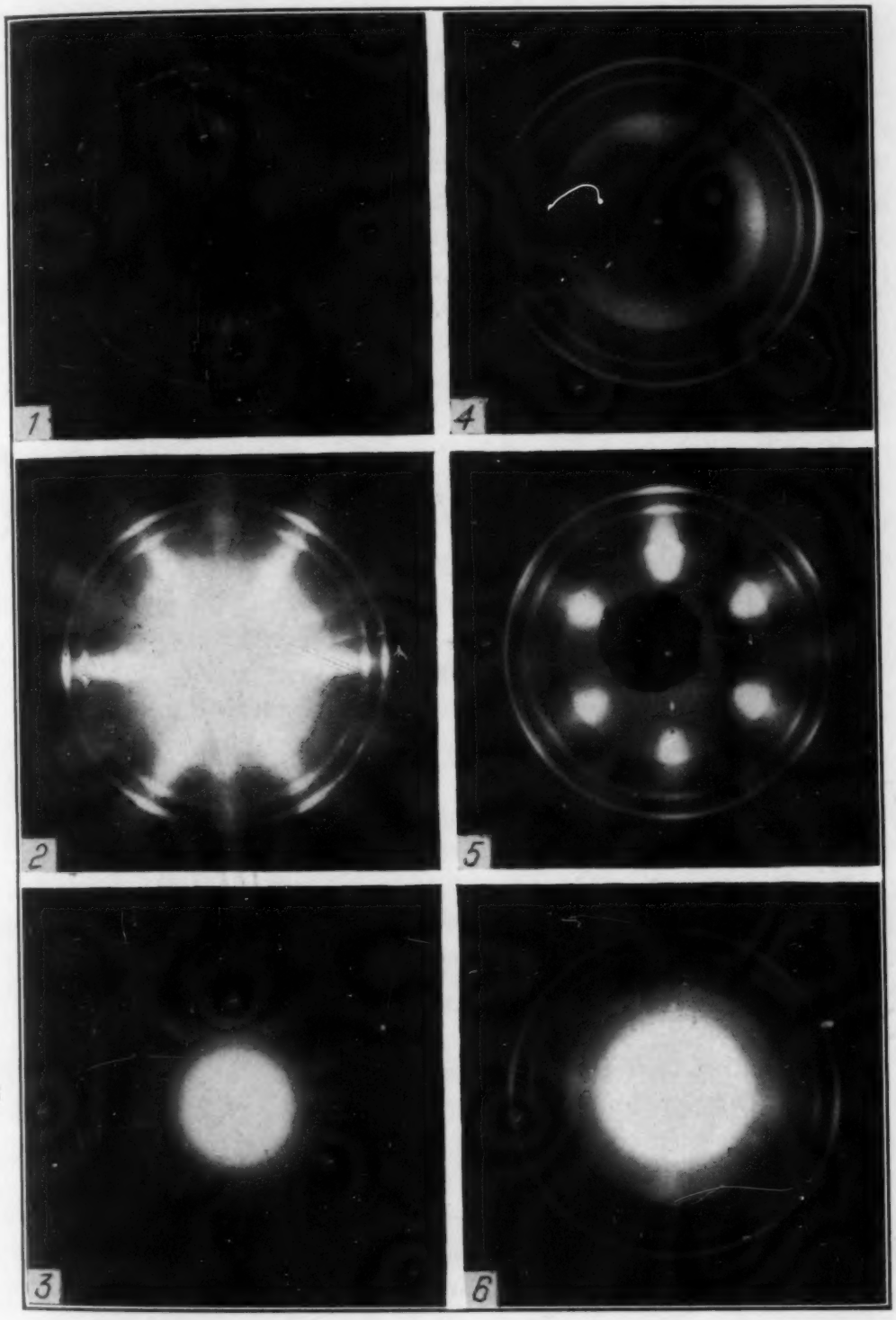


Fig. 2—Laue Diagrams Made of the Hot- and Cold-Rolled Strip in the N, P, and T Directions. 1, 2, and 3 Were Made of the Hot-Rolled Strip in the P, T, and N Directions Respectively. 4, 5, and 6 Were Made of the Cold-Rolled Strip in the P, T, and N Directions Respectively.

The corresponding X-ray patterns at a first glance are strikingly similar but on closer examination one can observe essential differences. The "T" diagrams of the hot- and cold-rolled strips are 6 point patterns but the hot-rolled strip exhibits an asterism which is more elongated radially and not as sharply defined. At first it was believed that this X-ray "T" diagram was characteristic only of the particular specimen, however, by making additional diagrams at other points in the "T" direction similar patterns were always obtained. This may be due to several causes, the orientation of the crystallites in the hot-rolled strip deviate considerably from the ideal orientation or else several orientation textures are present. These deductions, however, are mere speculation. However, the Laue diagrams definitely show that the hot working produced a strong fiber structure which in some respects is nearly as strong as that developed by cold rolling. The reflection method can, however, definitely settle the speculations deduced from a study of the Laue diagrams.

An interesting difference is exhibited by the "N" diagrams of the cold- and hot-rolled specimens. A definite orientation texture is exhibited in the cold-rolled specimen while in the hot-rolled "N" diagram the grains appear to be oriented at random. This may mean that the crystallites of the cold-rolled specimen are lined up more precisely in a definite direction while in the hot-rolled strip they are oriented at random about this direction. The other possibility is that the orientation textures of the hot- and cold-rolled strip differ. It can also be observed that the crystallites in the hot-rolled strip are larger. This is substantiated in the photomicrographs. Finally the "P" diagrams of the hot- and cold-rolled strips appear to have similar Laue diagrams. Here again the grains in the hot-rolled strip are definitely the larger.

In addition to this information the orientation textures common to both structures can be determined. However, the relative intensity of these orientation textures in the hot- and cold-rolled strips cannot be determined.

The "T" diagrams only exhibit the well-known orientations (2), but fail to reveal essential differences in orientation texture.

The following are orientation textures exhibited by these Laue diagrams.

Rolling Plane	In Rolling Direction
(100) (N)	[110] (P)
(211) (N)	[110] (P)

Surface Diffraction Diagrams of Hot-Rolled Strip. To determine other crystallographic orientations surface diffraction diagrams were made as already described and these are shown in Fig. 3. The "N", "T", and "P" diagrams are grouped so that direct comparison of corresponding patterns can be made.

The crystallographic structure of the hot-rolled strip will be analyzed first. The "N" reflection diagram made by setting the specimen at 10 degrees to the X-ray beam gave a strong (110) line. This shows that a new orientation is present for on comparing it with the cold-rolled specimen made under the same conditions the (110) line is found to be very weak; the Laue diagrams failed to show this. At 14 degrees "N" the (100) line is found to be weak and shows that only a very few (100) planes lie in the surface. At 17 degrees "N" the (211) line was found to be weak but somewhat stronger than the (100); therefore there are more (211) planes in the surface than (100) planes. At 28 degrees the (123) "N" line was found to be rather weak. The (111) "N" line was missing. It should also be observed that the (110) line is still very strong even when the specimen is set at 17 degrees. The orientation is therefore not an ideal one but varies over a small angular range. A comparison of the "N" diagrams indicates that several orientations are present in the hot-rolled strip.

To determine the crystallographic directions which lie in the "P" (parallel to rolling direction) and "T" directions (parallel to transverse rolling direction) similar sets of X-ray diagrams were made. These surface diffraction diagrams are also shown in Fig. 3 under "T" and "P".

In the "P" surface diffraction diagrams of the hot-rolled strip the (110) is very strong but the (100), (211) and (123) lines are of moderate intensity. This shows at once that several orientations are present with the following crystallographic directions coinciding with the rolling direction [110], [100], [211], [310], and [123]. Not all of these are necessarily due to grains oriented in this way but may be due to zonal axes which happen to coincide with the rolling direction and which is caused by deviations from the ideal orientations.

The surface diffraction diagrams of the "T" specimen show that the [110] is strongest in the transverse rolling direction. The [211], [310], and [123] axes also are present but only of moderate intensity, but the [100] and [111] directions are practically

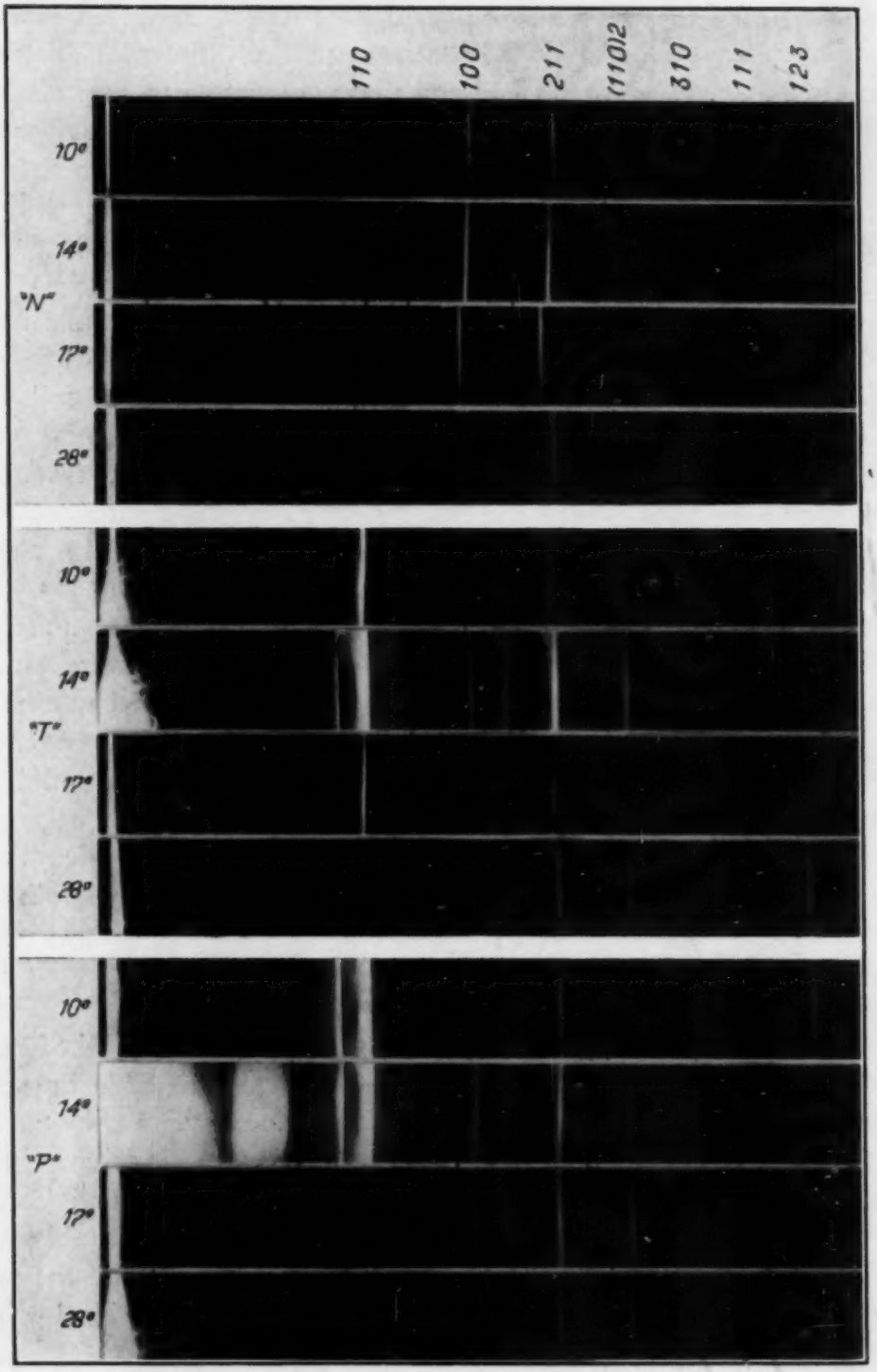


Fig. 3—Cold-Rolled Strip.

Fig. 3—The Angle of Incidence the X-ray Beam Makes with the Surface of the Specimen is Given for Each Diagram.

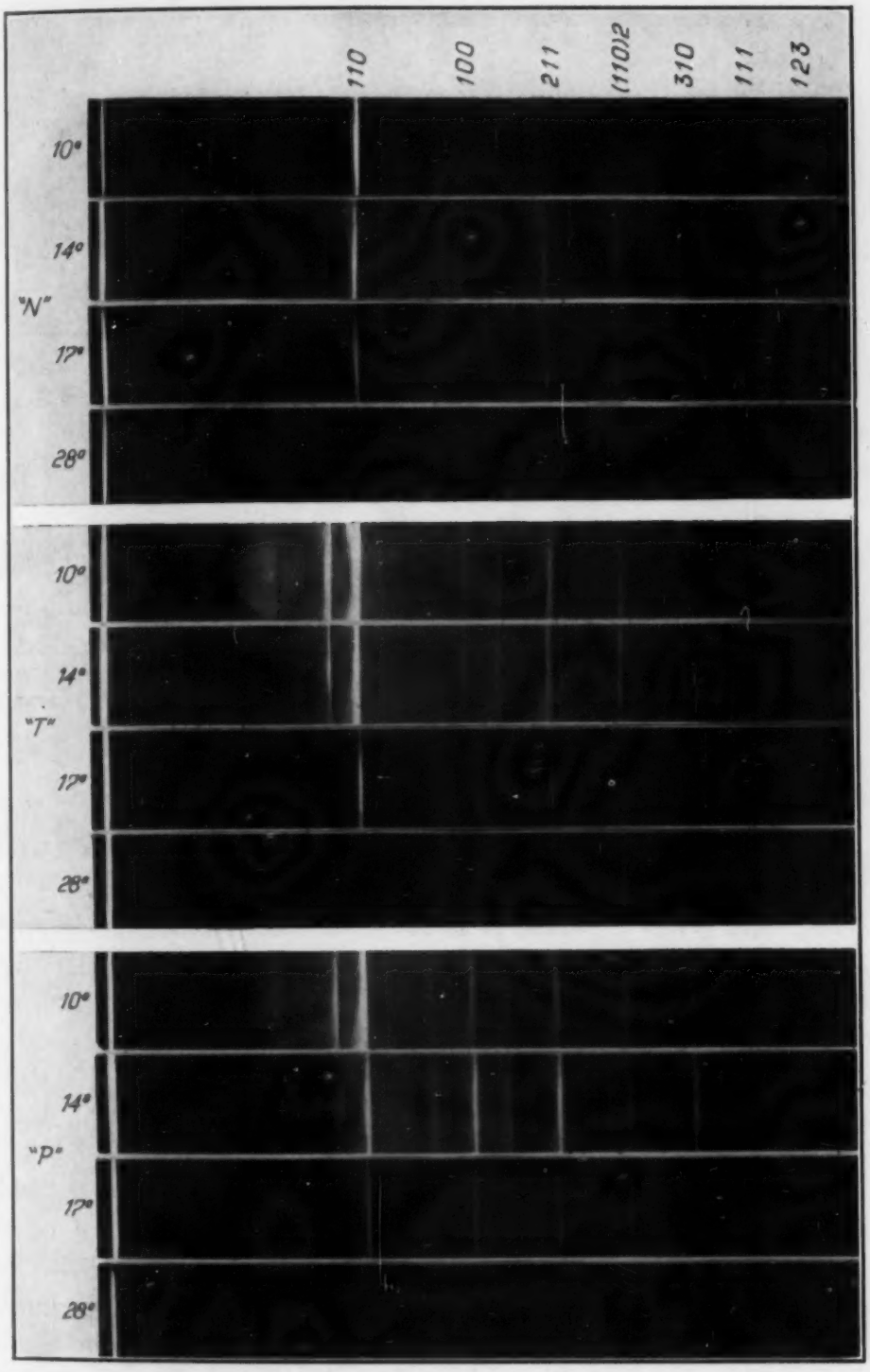


Fig. 3—Hot Strip.

Fig. 3—The Angle of Incidence the X-ray Beam Makes with the Surface of the Specimen is Given for Each Diagram.

missing. The absence of these lines eliminates the possibility of several orientations.

Analysis of Surface Diffraction Diagrams of the Cold-Rolled Strip. The cold-reduced strip was analyzed in the same manner and the results are shown in Table II along with the hot-rolled strip.

Table II

Relative Intensity of Diffraction Lines For Various Angles of Incidence

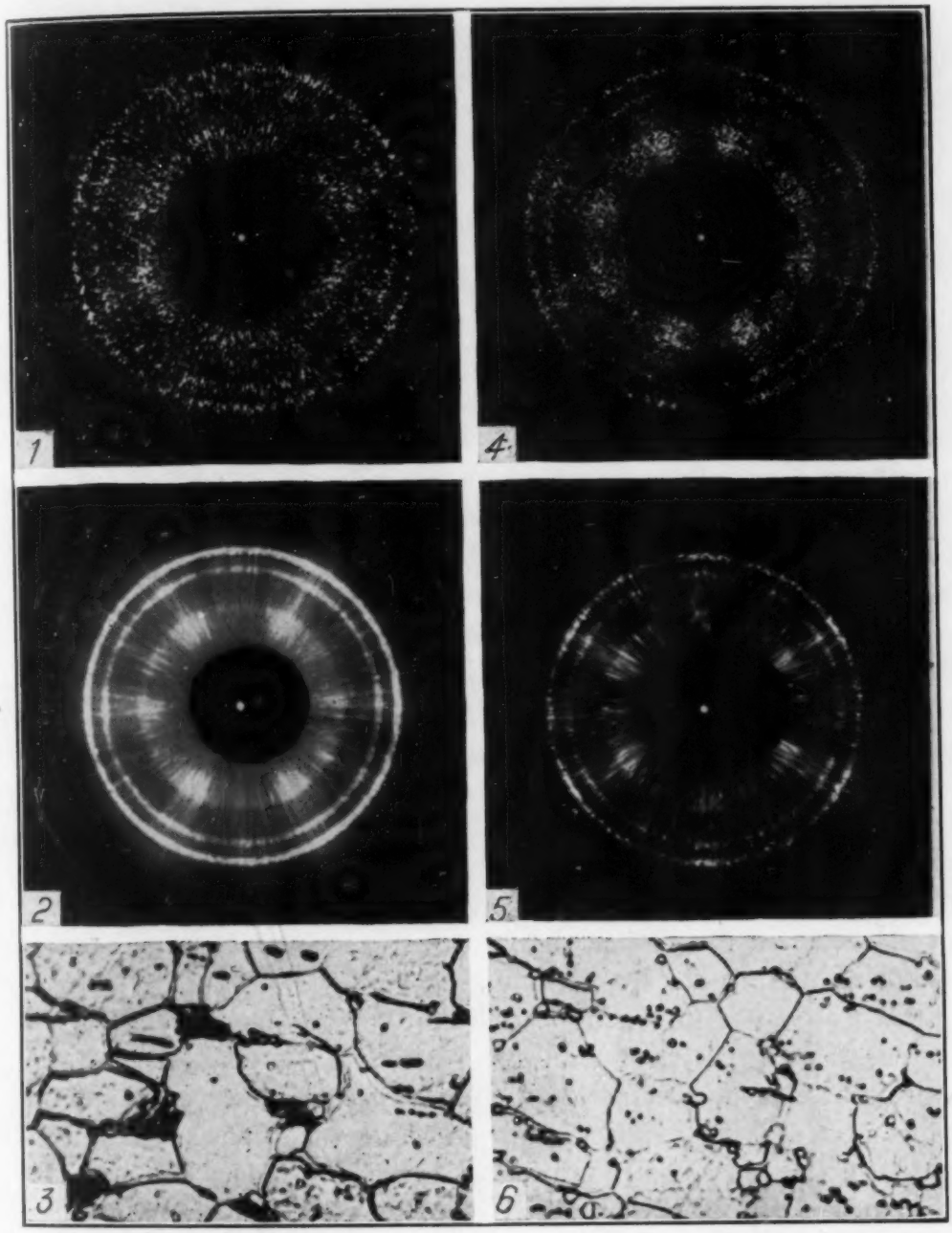
	(N) In Rolling Plane (Atomic Planes Which Lie In Surface)	
Plane	Hot-Rolled	Cold-Rolled
(110)	Very Strong	Weak
(100)	Weak	Strong
(211)	Weak	Strong
(111)	Missing	Weak
(123)	Weak	Weak
	"T" Crystallographic Axis Coinciding With The Transverse Rolling Direction	
[110]	Very Strong	Strong
[100]	Very weak or missing	Very Weak
[211]	Medium	Strong
[111]	Weak	Weak
[123]	Strong	Strong
	"P" Crystallographic Axis Coinciding With the Direction of Rolling	
[110]	Very Strong	Very Strong
[100]	Medium	Medium
[211]	Medium	Very Strong
[111]	Missing	Missing
[123]	Weak	Strong

Discussion of Results

The data given in Table II and the surface diffraction diagrams of Fig. 3 prove that there is a marked difference in the orientation texture of the hot- and cold-rolled strip, in fact, cold rolling has altered the fiber structure of the hot-rolled strip profoundly.

It is also rather surprising to find several crystallographic directions coinciding with the rolling direction, and of considerable intensity. The literature (2) only suggests that after hot and cold rolling the [110] direction is the fiber axis for hot- and cold-rolled strip steels. The present research proves that there are several others present. Also that the orientation texture of the hot- and cold-rolled strips differ considerably. The Laue diagrams of Fig. 2 hardly suggested these differences in fiber structures. By means of the surface diffraction method developed for investigations of this kind the most complex structure can easily be determined when studied systematically.

The object of this experiment was mainly performed to show



× 1000
1725 Degrees Fahr.

× 1000
1300 Degrees Fahr.

Fig. 4—Heat Treatment Failed to Remove the Directional Properties.

the differences existing in the fiber structures of the hot- and cold-rolled strip; however, it is possible to pick out a few orientations which are most likely present. These are given in Table III.

These results do not agree with Gensamer's (3). He was un-

Table III

Orientations Present In Hot-Rolled Low Carbon Strip When Rolled Between A_1 and A_3

Intensity	In The Rolling Plane	Rolling Direction
Very Strong	(110)	[100]
Strong	Various planes	[110]
Medium	Various planes	[123]
Medium	Various planes	[211]
Medium	Various planes	[310]
	Orientations Present In The Cold Reduced Strip	
Strong	(100)	[110]
Strong	(211)	[110]
Weak	Various planes	[123]
	Various planes	[310]
Very Weak	(110)	[100]

able to find any difference between the orientation textures of hot- and cold-rolled strip. However, this is to be expected since he depended entirely upon a modified Laue method which is inadequate when dealing with complex orientation textures.

The effect of heat treatment on the fiber structure of the cold-rolled strip is quite important. Can the directional properties developed during cold rolling be removed by heat treatment, especially when the fiber structure is so strongly developed?

The cold-reduced strip was heat treated at 1700 degrees Fahr. (925 degrees Cent.) for 2 minutes and air quenched, and another specimen was annealed at 1300 degrees Fahr. (705 degrees Cent.) for 1 hour and slowly cooled in the furnace. The X-ray Laue diagrams made in the "N" and "T" directions and the corresponding photomicrographs are shown in Fig. 4.

It was rather surprising to find that normalizing at 1700 degrees Fahr. (925 degrees Cent.) did not remove the directional properties entirely as a weak fiber structure still remains. However, the grains are completely recrystallized and quite uniform in size. The microstructure showed some indication of banding of the sorbite and the steel to be dirty. This may have something to do with the residual orientation texture.

Annealing at 1300 degrees Fahr. (705 degrees Cent.) was found to be less effective in removing the directional properties. The preferred orientation of the grains is much more intense and the grains appear to be smaller. A new recrystallization orientation texture is observed and this has been described in previous papers (1b). The photomicrograph shows the ferrite to be completely recrystallized and the carbides spheroidized.

Summary

1. Different orientations are developed in the hot-rolled and cold-rolled strip steels.

2. Cold rolling re-orients the fiber structure of the hot-rolled strip.

3. The Laue method is inadequate in dealing with complex orientation structures.

4. A new method using surface diffraction has been developed. It is very effective in showing differences in orientation textures and in the determination of the orientations as well.

5. The effect of heat treatment on the fiber structure of cold-reduced strip shows that it is quite difficult to remove the directional properties when they are strongly developed and especially when the microstructure exhibits banding and dirty steel.

Acknowledgment

The author wishes to acknowledge the assistance given by Robert Slee in the preparation of the specimens and X-ray diffraction diagrams.

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1. N. P. Goss, "Hot Working, Cold Working and Recrystallization Structures," Transactions, American Society for Metals, Dec. 1936. (a) Method of analysis, p. 987-995; (b) Twinning Textures, p. 1001.
2. Carpenter and Robertson, "Metals," Vol. I, Oxford, p. 127; Elam, "Distortion of Metal Crystals," p. 59.
3. Gensamer and Vukmanic, "Preferred Orientations in Hot-Rolled Low Carbon Steel," American Institute of Mining and Metallurgical Engineers, Iron and Steel Division, Vol. 125, 1937, p. 507.

DISCUSSION

J. T. MacKenzie, Jr.:[1] In the production of low carbon sheet for deep drawing purposes, box annealing after cold reduction often produces an elongated grain structure, as contrasted with the more usual equiaxed grain structure. I would like to ask the author if he has noticed any difference in the amount or type of preferred orientations in such elongated grain structures as compared to the orientations of similar materials but containing equiaxed grain structures. Also, does he think that a study, using his method, of the orientation of hot strip material prior to cold reduction and box annealing would give any indication of the final grain structure (i.e., equiaxed or elongated) after processing?

[1]Research Laboratory, United States Steel Corp., Kearny, N. J.

Author's Reply

In answer to Mr. MacKenzie as to the extent of preferred orientation present in box annealed strip showing elongated grains, usually elongated grains indicate preferred orientation in the strip but not always. To be absolutely sure that the elongated grains are oriented along the rolling direction one must of course depend upon the X-ray. It should be pointed out that even in box annealed strip showing equiaxed grains directional properties may be present. If the hot strip exhibits elongated grains the same is true. It can only be removed by heat treatment above A_3—and assuming the steel is reasonably clean.

Also if a hot strip exhibits strong directional properties and is then cold-rolled in excess of 60 per cent it will show a strong orientation texture and the microstructure may exhibit either equiaxed or elongated grains. A cold reduction of much less than 60 per cent given to a hot strip with a strong fiber structure and box annealed will also exhibit directional properties. The effect is of course accumulative.

THE EFFECT OF MOLYBDENUM AND COLUMBIUM ON THE STRUCTURE, PHYSICAL PROPERTIES AND CORROSION RESISTANCE OF AUSTENITIC STAINLESS STEELS

By Russell Franks, W. O. Binder and C. R. Bishop

Abstract

Briefly, this investigation has shown that low-carbon steels containing between 16 and 25 per cent chromium, 8 and 22 per cent nickel, and from 1 to 4 per cent molybdenum should contain, as shown in the structural diagrams, certain percentages of chromium, nickel and molybdenum to avoid formation of the sigma phase, especially when the steels are stress-relieved at 870 degrees Cent. (1600 degrees Fahr.). It is important to avoid sigma formation in order to preserve toughness. If the molybdenum content is kept between about 1.50 and 2.25 per cent with 18 to 19 per cent chromium and 12 to 14 nickel, a steel practically free of sigma is obtained. Such steels have satisfactory hot workability, high toughness and good resistance to pitting and oxidizing media as well as improved resistance to the reducing media, such as sulphuric acid and acetic acid vapors and condensates.

The steels containing 1.50 to 2.25 per cent molybdenum are subject to intergranular corrosion. To obtain optimum resistance to intergranular attack their columbium content should be at least ten times the carbon content but in most instances a columbium content of at least six times the carbon content will suffice. The steels containing even the lower ratio of columbium to carbon can be stress-relieved without loss of general corrosion resistance and are practically immune to intergranular attack, which renders them suitable for fabrication into vessels and other articles that require stress relief.

IN experiments made to enhance the resistance of the 18 per cent chromium-8 per cent nickel type of steel to pit and contact corrosion, which occur during exposure to weak acid solutions and solutions containing chlorides, additions of between 1 and 4

A paper presented before the Twenty-second Annual Convention of the Society held in Cleveland, October 21 to 25, 1940. The authors are associated with the Union Carbide and Carbon Research Laboratories, Inc., Niagara Falls, N. Y. Manuscript received June 21, 1940.

per cent molybdenum were found to be of great help. As the molybdenum content was increased with proportionate increases in nickel content, the steels became more difficult to hot work, and great precaution was required in forging and rolling even small ingots to avoid tearing and checking at the edges. It was further noted that when the higher molybdenum (above 2.50 per cent) steels were cooled slowly from the annealing temperatures or stress-relieved at 870 degrees Cent. (1600 degrees Fahr.) they became entirely nonmagnetic even though they were quite magnetic when rapidly cooled from annealing temperatures in the neighborhood of 1150 degrees Cent. (2100 degrees Fahr.). A decrease in resistance to corrosion accompanied this change in magnetic properties. Columbium additions made to the steels were found to eliminate susceptibility to intergranular attack but as before, the steels did not function like true austenitic materials; i. e., they became less magnetic under heating conditions that should normally render them more magnetic. Thus the phenomenon noted did not relate directly to carbide precipitation, but appeared to concern changes in the iron chromium-nickel system as a result of the molybdenum addition.

It was appreciated that molybdenum was a strong ferrite-forming element and that in the study to be made a wide range in nickel content would have to be investigated to attain austenitic conditions as the molybdenum and chromium contents were increased. The chromium range selected for study was 16 to 25 per cent, the individual chromium contents being approximately 16, 18, 20, 23, and 25 per cent. To each chromium content was added from 1 to 1.5, 1.75 to 2.25, and 2.75 to 3.25 per cent molybdenum, and various percentages of nickel to obtain steels wholly and partly austenitic. One-half per cent silicon and 1.50 per cent manganese were incorporated in most of the steels to obtain metal of good quality, and the carbon content was not allowed to exceed about 0.10 per cent.

A similar series of steels was made in which columbium was added. The columbium content varied between seven and fourteen times the carbon content, also with a maximum carbon content of 0.10 per cent. All the steels were melted in a basic-lined high frequency induction furnace using 10- to 20-pound charges. The ingots obtained were forged and rolled into ¼-inch thick plates from which samples approximately 1 inch wide by 1.5 inch long were secured.

Samples of each steel were examined for structural character-

istics at room temperature, after heating for 5 to 10 minutes in the range 1100 to 1150 degrees Cent. (2010 to 2100 degrees Fahr.) and air cooling, and after heating in the same range followed by treatment for four hours at 870 degrees Cent. (1600 degrees Fahr.) and air cooling. Other samples of the steels were similarly treated at 1100 to 1150 degrees Cent. (2010 to 2100 degrees Fahr.) and at 870 degrees Cent. (1600 degrees Fahr.) and subsequently held four hours at 650 degrees Cent. (1200 degrees Fahr.) and air cooled. This latter treatment did not greatly alter the structure from that

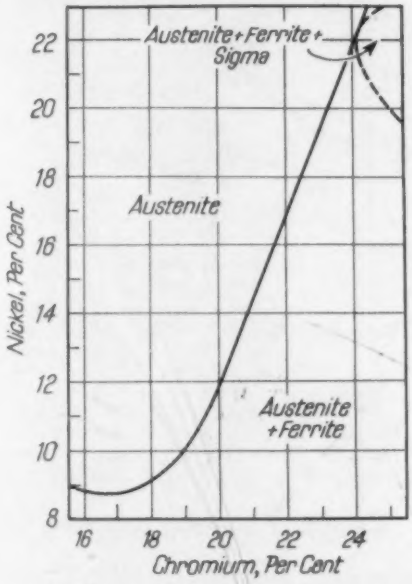

Fig. 1—Structural Diagram for Chromium-Nickel Steels Containing 1 to 1.5 Per Cent Molybdenum and a Maximum of 0.10 Per Cent Carbon After Air Cooling from 1100 to 1150 Degrees Cent. (2010 to 2100 Degrees Fahr.).

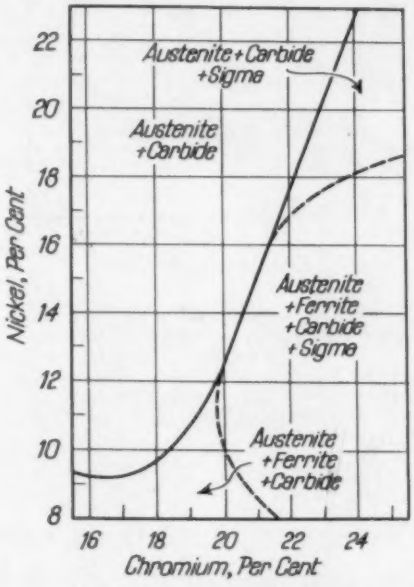

Fig. 2—Structural Diagram for Chromium-Nickel Steels Containing 1 to 1.5 Per Cent Molybdenum and a Maximum of 0.10 Per Cent Carbon After Air Cooling from 1100 to 1150 Degrees Cent. (2010 to 2100 Degrees Fahr.), and Reheating 4 Hours at 870 Degrees Cent. (1600 Degrees Fahr.) and Air Cooling.

obtained by the air cool from 1100 to 1150 degrees Cent. (2010 to 2100 degrees Fahr.) followed by holding at 870 degrees Cent. (1600 degrees Fahr.), and the discussion of its effect will be deferred until later.

The samples given the two first-mentioned heat treatments were examined for magnetism using a magnetic balance accurately enough to note a magnetic pull of a few milligrams, to determine whether a given steel was magnetic, slightly magnetic, or nonmagnetic. In addition the samples were examined metallographically after etching with 50 parts hydrochloric acid, 5 parts nitric acid, and 45 parts water, at

a magnification of 100 and 500 diameters to study the structure existing at room temperature after the respective heat treatments.

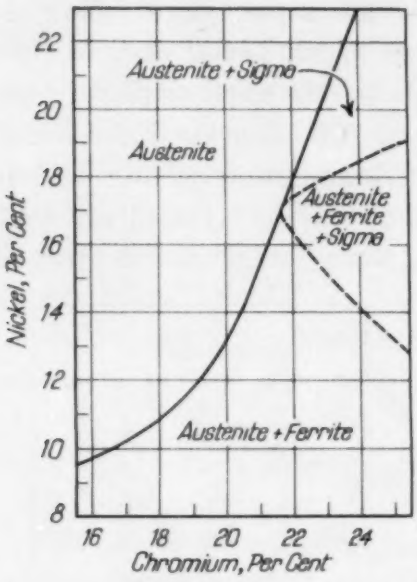

Fig. 3—Structural Diagram for Chromium-Nickel Steels Containing 1.75 to 2.25 Per Cent Molybdenum and a Maximum of 0.10 Per Cent Carbon After Air Cooling from 1100 to 1150 Degrees Cent. (2010 to 2100 Degrees Fahr.).

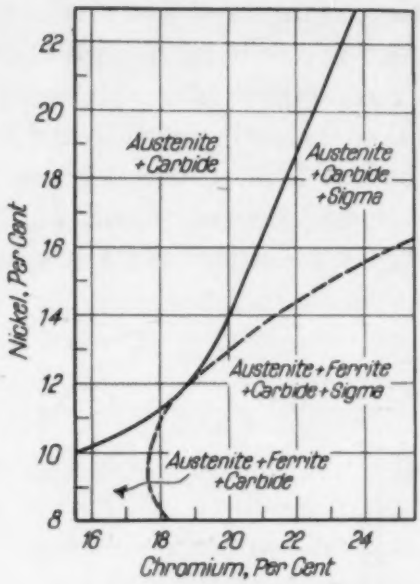

Fig. 4—Structural Diagram for Chromium-Nickel Steels Containing 1.75 to 2.25 Per Cent Molybdenum and a Maximum of 0.10 Per Cent Carbon After Air Cooling from 1100 to 1150 Degrees Cent. (2010 to 2100 Degrees Fahr.) and Reheating 4 Hours at 870 Degrees Cent. (1600 Degrees Fahr.) and Air Cooling.

The compositions of the steels containing molybdenum investigated in this manner are given in Table I, and their structures as determined magnetically and metallographically yielded the information given in Figs. 1 to 6.

The structural diagrams of Figs. 1 to 6 were constructed by plotting the chromium and nickel contents along the co-ordinates and

Table I

Compositions of Molybdenum-Bearing Chromium-Nickel Steels Examined Structurally

Heat No.	Per Cent					
	Chromium	Nickel	Molybdenum	Manganese	Silicon	Carbon
*E664	16.00	8.70	1.25	1.50	0.40	0.07
*E528	16.00	10.00	1.00	1.50	0.40	0.07
E399	15.98	11.93	0.99	1.60	0.43	0.04
E412	15.75	11.94	0.92	1.58	0.41	0.05
E458	16.11	11.93	0.98	1.62	0.40	0.07
C724	17.58	9.12	1.06	0.10	0.34	0.10
C79	18.14	8.37	1.17	3.26	0.49	0.07
*C4	18.00	9.00	1.00	0.50	0.40	0.09
D229	18.45	10.24	0.90	0.57	0.35	0.04
E69	18.25	12.09	1.29	1.55	0.50	0.08
E456	18.04	11.89	1.59	1.57	0.44	0.07

*Approximate composition with exception of carbon content.

Table I—(Continued)

	Per Cent					
Heat No.	Chromium	Nickel	Molybdenum	Manganese	Silicon	Carbon
E396	18.22	12.03	1.53	1.66	0.44	0.05
E400	19.84	13.74	0.98	1.61	0.45	0.06
*E540	20.00	11.00	1.00	1.50	0.40	0.06
*E667	21.00	14.00	1.25	1.50	0.40	0.10
*E668	21.00	16.00	1.25	1.50	0.40	0.08
E401	23.53	14.02	0.99	1.67	0.48	0.07
E470	23.36	14.00	1.00	1.60	0.49	0.08
E426	23.35	15.25	1.01	1.63	0.53	0.07
E428	23.73	21.05	1.01	1.62	0.48	0.08
*E642	23.00	20.00	1.00	1.50	0.40	0.08
*E666	16.00	9.00	2.00	1.50	0.40	0.08
*E665	16.00	10.50	2.00	1.50	0.40	0.08
*E529	16.00	12.00	2.00	1.50	0.40	0.05
D818	15.74	13.68	2.28	1.49	0.44	0.09
D835	15.95	13.84	1.72	1.50	0.45	0.07
B927	18.20	8.72	2.20	0.56	0.53	0.10
C80	18.32	8.91	2.20	3.19	0.45	0.10
D228	18.45	10.35	2.18	0.57	0.38	0.06
*E537	18.00	10.50	2.00	1.50	0.40	0.06
D820	18.04	13.73	1.72	1.48	0.48	0.06
D821	18.02	13.75	2.18	1.52	0.51	0.07
E397	18.13	13.75	2.07	1.59	0.44	0.06
E457	17.93	13.83	2.00	1.62	0.45	0.08
D824	19.80	13.66	1.72	1.51	0.26	0.07
*E669	21.00	16.00	2.00	1.50	0.40	0.09
*E545	22.00	9.00	2.00	1.50	0.40	0.06
*E670	22.00	17.00	2.00	1.50	0.40	0.10
D832	22.74	13.60	1.79	1.60	0.45	0.07
D833	23.08	13.92	2.08	1.59	0.50	0.07
*E548	23.00	16.00	2.00	1.50	0.40	0.06
E427	23.35	18.08	2.27	1.63	0.60	0.10
*E643	23.00	21.00	2.00	1.50	0.40	0.06
*E552	24.00	14.00	2.00	1.50	0.40	0.06
*E553	24.00	22.00	2.00	1.50	0.40	0.08
E429	25.34	19.90	2.21	1.73	0.56	0.10
D819	15.70	13.68	3.15	1.50	0.51	0.08
*E534	17.00	12.00	3.00	1.50	0.40	0.05
B979	18.22	8.64	4.15	*0.50	*0.50	0.11
D141	18.19	9.20	3.70	0.63	0.48	0.07
C922	18.30	9.58	3.26	0.46	0.47	0.05
C733	17.96	11.87	3.12	1.60	0.46	0.04
*E538	18.00	12.00	3.00	1.50	0.40	0.06
Type 317	17.92	13.61	3.30	1.87	0.37	0.07
D823	17.95	13.80	2.96	1.56	0.56	0.08
E413	18.20	14.76	3.37	1.63	0.42	0.06
E402	18.13	14.91	3.12	1.63	0.50	0.08
E471	18.18	17.97	3.59	1.65	0.42	0.08
D825	19.86	13.82	2.76	1.53	0.53	0.06
D826	20.00	13.82	3.12	1.48	0.48	0.09
E419	20.38	16.32	3.36	1.62	0.51	0.06
*E541	21.00	15.00	3.00	1.50	0.40	0.06
*E542	21.00	17.00	3.00	1.50	0.40	0.06
D834	22.92	13.78	2.60	1.66	0.53	0.07
*E549	23.00	16.00	3.25	1.50	0.40	0.06
*E550	23.00	20.00	3.00	1.50	0.40	0.07
*E644	23.00	22.00	3.00	1.50	0.40	0.09
*E554	24.00	22.00	3.00	1.50	0.40	0.09
E430	25.31	19.97	3.31	1.60	0.55	0.08

*Approximate composition with exception of carbon content.

holding the molybdenum contents in the ranges 1 to 1.50, 1.75 to 2.25, and 2.75 to 3.25 per cent for the three different series of steels. As previously stated, the carbon, manganese and silicon contents of the steels were kept fairly constant and the effects of the different

percentages of molybdenum on the structures of the steels are illustrated.

A study of these structural diagrams shows that depending on the amount of iron, chromium, nickel, and molybdenum present in the alloy it is possible to obtain steels consisting of austenite, austenite + ferrite, austenite + ferrite + sigma, and austenite + sigma even after air cooling from 1100 to 1150 degrees Cent. (2010

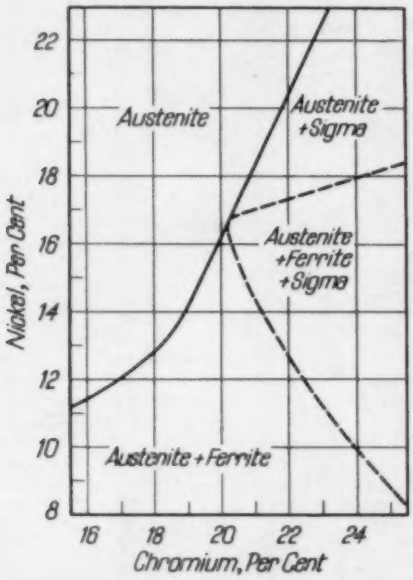

Fig. 5—Structural Diagram for Chromium-Nickel Steels Containing 2.75 to 3.25 Per Cent Molybdenum and a Maximum of 0.10 Per Cent Carbon After Air Cooling from 1100 to 1150 Degrees Cent. (2010 to 2100 Degrees Fahr.).

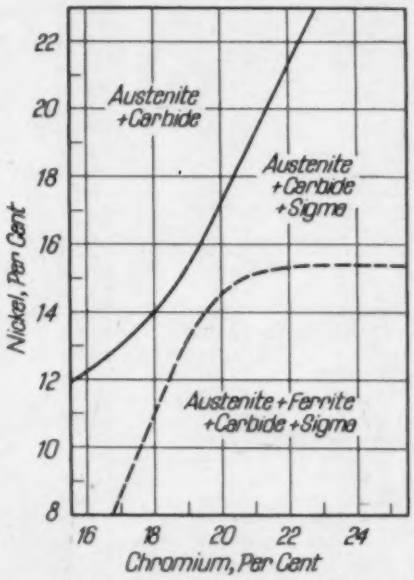

Fig. 6—Structural Diagram for Chromium-Nickel Steels Containing 2.75 to 3.25 Per Cent Molybdenum and a Maximum of 0.10 Per Cent Carbon After Air Cooling from 1100 to 1150 Degrees Cent. (2010 to 2100 Degrees Fahr.) and Reheating 4 Hours at 870 Degrees Cent. (1600 Degrees Fahr.) and Air Cooling.

to 2100 degrees Fahr.). The presence of the sigma phase (1), (2) in the samples so heat treated was determined by the appearance of the constituent as noted in the metallographic examination of these samples, and others to be later described, which were heated at 870 degrees Cent. (1600 degrees Fahr.). The similarity in the appearance of the constituent in both sets of samples was sufficient to establish its presence in the samples heated at 1100 to 1150 degrees Cent. (2010 to 2100 degrees Fahr.). It is shown that as the molybdenum content is increased from about 1 to somewhat over 3 per cent, it is necessary to increase the nickel content with a given chromium content, to maintain an austenitic structure. This means that as the molybdenum content increases there is a gradual shift of the austenite

line to the left, which decreases the area of the austenite field with a broadening of the fields representing the steels containing austenite + ferrite; austenite + ferrite + sigma; and austenite + sigma. However, when the molybdenum content is in the range 2.75 to 3.25 per cent, the austenite + ferrite field is almost eliminated with enlargement of the areas of the austenite + ferrite + sigma and austenite + sigma fields. The boundaries of all the fields except the

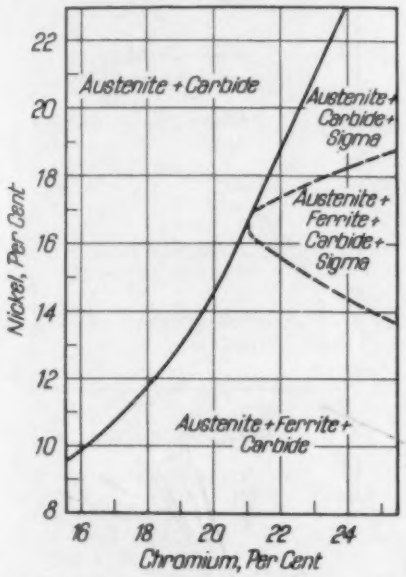

Fig. 7—Structural Diagram for Chromium-Nickel Steels Containing 1 to 1.5 Per Cent Molybdenum, a Maximum of 0.10 Per Cent Carbon, and Seven to Fourteen Times as Much Columbium as Carbon After Air Cooling from 1100 to 1150 Degrees Cent. (2010 to 2100 Degrees Fahr.).

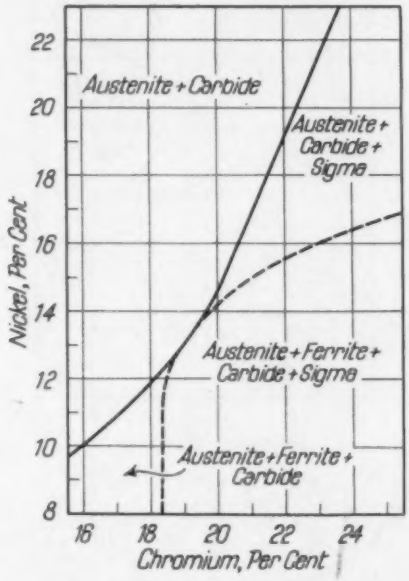

Fig. 8—Structural Diagram for Chromium-Nickel Steels Containing 1 to 1.5 Per Cent Molybdenum, a Maximum of 0.10 Per Cent Carbon, and Seven to Fourteen Times as Much Columbium as Carbon After Air Cooling from 1100 to 1150 Degrees Cent. (2010 to 2100 Degrees Fahr.) and Reheating 4 Hours at 870 Degrees Cent. (1600 Degrees Fahr.) and Air Cooling.

austenite are dotted because the exact location of these regions has not been definitely established.

Heating the steels for only four hours at 870 degrees Cent. (1600 degrees Fahr.) after treatment at the higher temperatures, 1100 to 1150 degrees Cent. (2010 to 2100 degrees Fahr.) causes the appearance of a carbide constituent in addition to the already existing phases; also heating at 870 degrees Cent. (1600 degrees Fahr.) causes a shift in the austenite line to the left, with a narrowing of the austenite + carbide field. The presence of sigma after heating at this temperature was readily detected with the magnetic balance. Many of the steels investigated contained ferrite that was

magnetic and identified under the microscope, but after heating at 870 degrees Cent. (1600 degrees Fahr.) they either lost considerable magnetism or became completely nonmagnetic depending on their composition, showing conclusively the presence of sigma constituent.

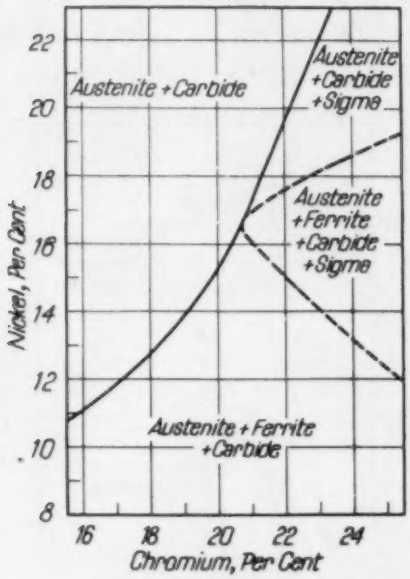

Fig. 9—Structural Diagram for Chromium-Nickel Steels Containing 1.75 to 2.25 Per Cent Molybdenum, a Maximum of 0.10 Per Cent Carbon, and Seven to Fourteen Times as Much Columbium as Carbon After Air Cooling from 1100 to 1150 Degrees Cent. (2010 to 2100 Degrees Fahr.).

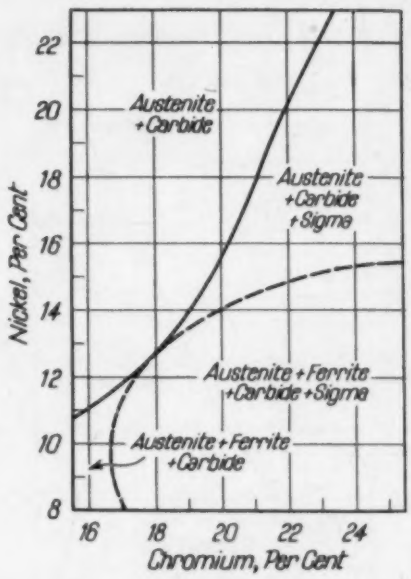

Fig. 10—Structural Diagram for Chromium-Nickel Steels Containing 1.75 to 2.25 Per Cent Molybdenum, a Maximum of 0.10 Per Cent Carbon, and Seven to Fourteen Times as Much Columbium as Carbon After Air Cooling from 1100 to 1150 Degrees Cent. (2010 to 2100 Degrees Fahr.) and Reheating 4 Hours at 870 Degrees Cent. (1600 Degrees Fahr.) and Air Cooling.

Table II

Compositions of Molybdenum and Columbium-Bearing Chromium-Nickel Steels Examined Structurally

Heat No.	Per Cent						
	Chromium	Nickel	Molybdenum	Manganese	Silicon	Columbium	Carbon
D640	16.07	9.87	1.61	1.54	0.34	0.60	0.07
D641	16.17	11.89	1.62	1.56	0.37	0.56	0.08
D642	16.12	13.49	1.60	1.55	0.38	0.56	0.08
*E530	17.00	10.00	1.00	1.50	0.40	0.70	0.10
*E531	17.00	11.00	1.00	1.50	0.40	0.70	0.06
D645	18.11	10.04	1.55	1.55	0.37	0.58	0.08
E404	18.25	10.40	1.53	1.69	0.54	0.72	0.07
*E539	18.00	11.00	1.00	1.50	0.40	0.70	0.06
E 74	17.97	11.84	1.08	1.50	0.48	0.56	0.08
E274	18.41	10.94	0.99	1.52	0.61	0.89	0.07
E312	18.03	12.11	1.63	1.60	0.46	0.78	0.05
D646	18.36	12.01	1.60	1.55	0.32	0.56	0.06
D647	18.33	13.87	1.57	1.53	0.30	0.58	0.08
E405	18.22	14.00	1.52	1.64	0.52	0.72	0.07
D650	19.91	9.95	1.51	1.56	0.35	0.52	0.07
E420	19.11	13.62	1.59	1.65	0.45	0.70	0.06

*Approximate composition except for carbon content.

Table II—(Continued)

Heat No.	Per Cent						
	Chromium	Nickel	Molybdenum	Manganese	Silicon	Columbium	Carbon
D651	20.14	12.05	1.57	1.56	0.36	0.59	0.08
D652	20.08	14.04	1.57	1.49	0.35	0.57	0.09
D653	20.26	16.18	1.58	1.50	0.25	0.58	0.08
*E546	22.00	16.00	1.00	1.50	0.40	0.70	0.07
E424	23.52	15.70	1.28	1.71	0.56	1.02	0.09
*E551	23.00	18.00	1.50	1.50	0.40	0.70	0.07
*E645	23.00	21.00	1.00	1.50	0.40	0.70	0.08
E431	25.69	19.87	0.90	1.73	0.61	0.97	0.11
*E532	17.00	11.00	2.00	1.50	0.40	0.70	0.07
*E533	17.00	12.00	2.00	1.50	0.40	0.70	0.05
C379	18.60	9.19	2.38	*1.25	*0.60	0.83	0.07
D325	18.14	10.03	2.03	1.54	0.35	0.77	0.09
D657	18.40	11.76	2.03	1.56	0.33	0.40	0.07
E309	17.90	12.04	1.99	1.54	0.45	0.87	0.06
E416	18.40	12.51	2.00	1.64	0.48	0.69	0.06
E408	18.23	12.47	2.00	1.69	0.55	0.75	0.08
E275	17.79	12.95	2.02	1.52	0.66	0.95	0.07
E409	18.21	13.42	2.02	1.65	0.53	0.75	0.07
E478	18.31	13.48	2.04	1.72	0.56	0.75	0.06
D327	17.73	13.85	2.04	1.52	0.42	0.74	0.07
D655	18.28	14.25	2.03	1.49	0.31	0.46	0.08
D328	17.91	15.82	2.06	1.53	0.39	0.77	0.06
E 9	19.01	12.77	1.96	2.14	0.48	0.56	0.07
E421	19.59	15.02	2.05	1.70	0.52	0.72	0.06
*E547	22.00	16.00	2.00	1.50	0.40	0.70	0.07
D369	23.28	12.06	2.18	1.56	0.45	0.71	0.08
D370	23.31	13.81	2.04	1.55	0.44	0.73	0.07
D371	23.51	15.71	2.05	1.56	0.42	0.73	0.08
D372	23.23	17.89	2.05	1.54	0.44	0.78	0.07
D373	23.80	20.06	2.05	1.51	0.46	0.75	0.07
*E646	23.00	22.00	2.00	1.50	0.40	0.80	0.10
E432	25.29	20.06	2.07	1.74	0.64	0.97	0.11
D353	15.89	9.73	3.15	1.54	0.35	0.73	0.08
D354	16.09	11.77	3.13	1.52	0.34	0.73	0.06
D355	16.11	13.81	2.95	1.51	0.36	0.66	0.08
D356	16.15	15.99	3.01	1.52	0.37	0.66	0.05
*E535	17.00	12.00	3.00	1.50	0.40	0.70	0.06
*E536	17.00	13.00	3.00	1.50	0.40	0.70	0.05
D329	17.85	10.51	3.02	1.52	0.46	0.76	0.06
D330	17.91	11.87	3.09	1.49	0.48	0.68	0.07
D331	17.97	13.85	3.19	1.46	0.40	0.75	0.07
D332	17.68	15.78	3.19	1.51	0.46	0.73	0.06
D361	19.08	13.81	3.09	1.48	0.36	0.73	0.10
E238	18.74	16.09	3.31	2.18	0.49	0.50	0.07
E410	18.51	17.93	3.50	1.64	0.59	0.75	0.08
D392	19.74	10.09	2.96	1.56	0.21	0.69	0.07
D379	19.54	11.69	3.00	1.51	0.40	0.73	0.07
D380	19.54	16.13	3.00	1.50	0.40	0.71	0.06
E422	19.81	18.08	3.10	1.72	0.44	0.75	0.07
*E543	21.50	16.00	3.00	1.50	0.40	0.70	0.07
*E544	21.50	18.00	3.00	1.50	0.40	0.70	0.07
E425	23.62	19.90	3.23	1.69	0.53	1.02	0.07
E647	23.00	23.00	3.00	1.50	0.40	0.80	0.10
E433	24.86	20.39	3.19	1.69	0.61	0.99	0.09

*Approximate composition except for carbon content.

In fact, when the molybdenum content was in the range 2.75 to 3.25 per cent, the ferritic constituent became so unstable that during the heating it was either partially or totally converted to sigma thereby eliminating the austenite-ferrite-carbide field in the composition studied. The data given in these diagrams finally show that as the chromium content is increased the influence of molybdenum in causing sigma formation is intensified.

The series of chromium-nickel steels containing both molybdenum and columbium was studied similarly for structural characteristics. The compositions of the steels used in this part of the investigation are given in Table II and their structures are described in Figs. 7 to 12.

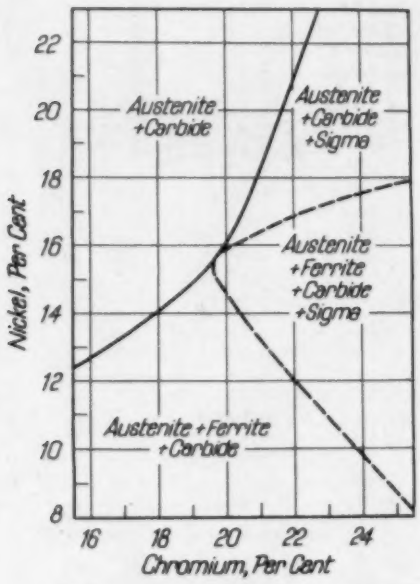

Fig. 11—Structural Diagram for Chromium-Nickel Steels Containing 2.75 to 3.25 Per Cent Molybdenum, a Maximum of 0.10 Per Cent Carbon, and Seven to Fourteen Times as Much Columbium as Carbon After Air Cooling from 1100 to 1150 Degrees Cent. (2010 to 2100 Degrees Fahr.).

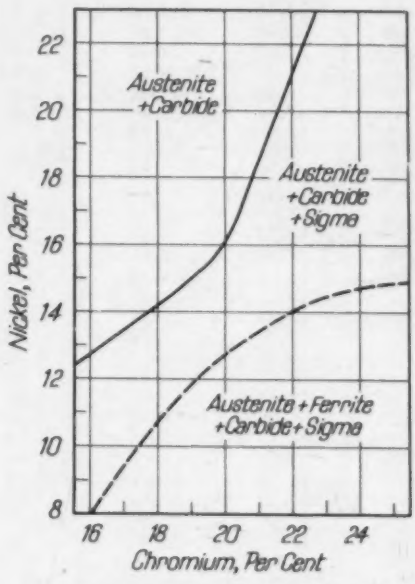

Fig. 12—Structural Diagram for Chromium-Nickel Steels Containing 2.75 to 3.25 Per Cent Molybdenum, a Maximum of 0.10 Per Cent Carbon, and Seven to Fourteen Times as Much Columbium as Carbon After Air Cooling from 1100 to 1150 Degrees Cent. (2010 to 2100 Degrees Fahr.) and Reheating 4 Hours at 870 Degrees Cent. (1600 Degrees Fahr.) and Air Cooling.

As illustrated by the diagrams of Figs. 7 to 12, adding columbium to the molybdenum-containing chromium-nickel steels did not prevent sigma (3) formation but instead aided somewhat in the formation of this constituent. The extent to which columbium influenced sigma formation is not clear. The amount of columbium added was sufficient to combine with the carbon present, and the influence of columbium carbide on sigma formation is not known. It is suspected that the columbium addition would make a given amount of molybdenum more effective because it would prevent the formation of molybdenum carbide and allow all the molybdenum present to go into solid solution and exert full influence. On the other hand, this should make a given percentage of molybdenum more influential from the standpoint of corrosion resistance.

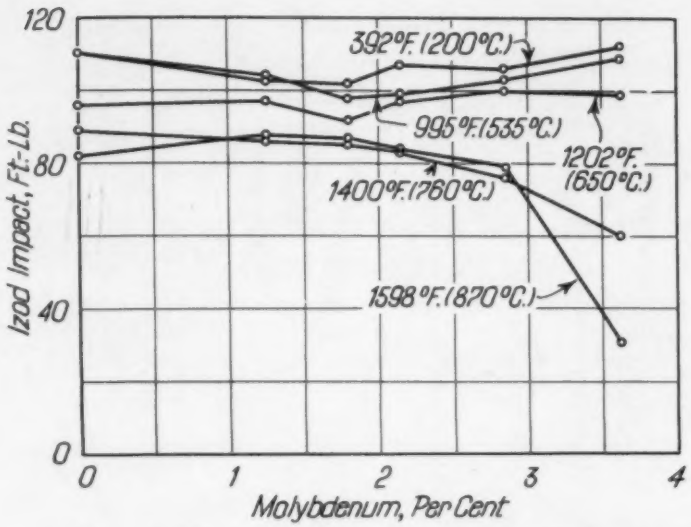

Fig. 13—Effect of 72 Hours' Exposure at Temperatures Between 200 Degrees Cent. (392 Degrees Fahr.) and 870 Degrees Cent. (1600 Degrees Fahr.) On Impact Toughness of Molybdenum-Bearing Chromium-Nickel Steels. The Steels Were Air-Cooled from 1100 Degrees Cent. (2010 Degrees Fahr.) Prior to Exposure to the Holding Temperature.

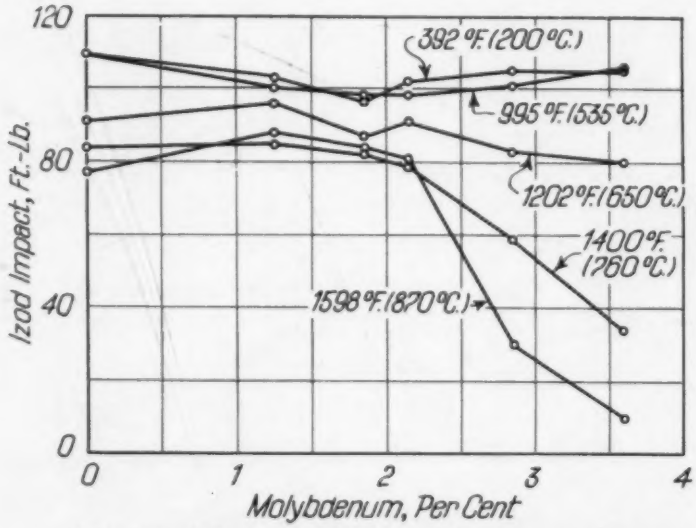

Fig. 14—Effect of 350 Hours' Exposure at Temperatures Between 200 Degrees Cent. (392 Degrees Fahr.) and 870 Degrees Cent. (1600 Degrees Fahr.) On Impact Toughness of Molybdenum-Bearing Chromium-Nickel Steels. The Steels Were Air-Cooled from 1100 Degrees Cent. (2010 Degrees Fahr.) Prior to Exposure to the Holding Temperature.

With columbium present it is necessary to increase the nickel content with given amounts of molybdenum and chromium to attain a fully austenitic structure after air cooling from 1100 to 1150 degrees Cent. (2010 to 2100 degrees Fahr.). The structures of the steels also contain carbides because most of the columbium carbide

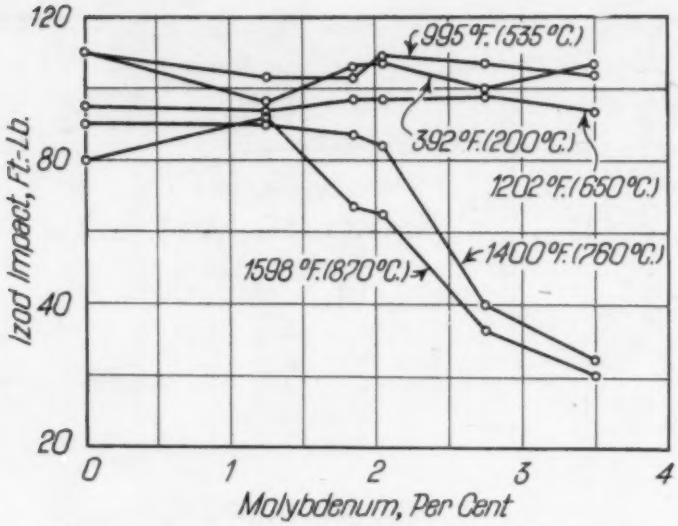

Fig. 15—Effect of 72 Hours' Exposure at Temperatures Between 200 Degrees Cent. (392 Degrees Fahr.) and 870 Degrees Cent. (1600 Degrees Fahr.) On Impact Toughness of Molybdenum and Columbium-Bearing Chromium-Nickel Steels. The Steels Were Air-Cooled from 1100 Degrees Cent. (2010 Degrees Fahr.) Prior to Exposure to the Holding Temperature.

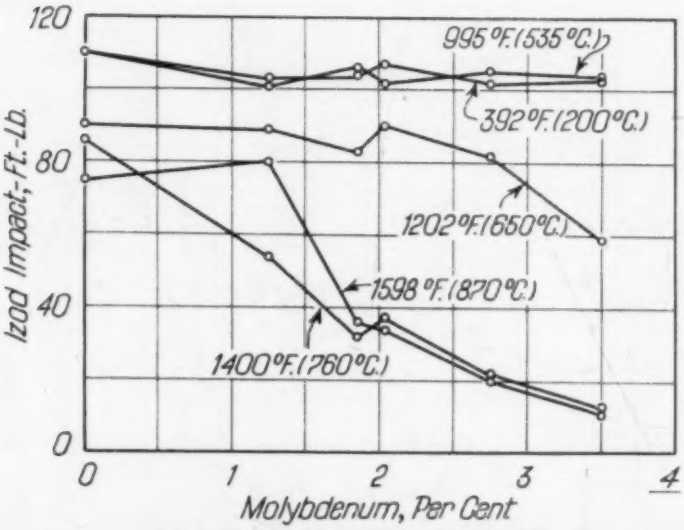

Fig. 16—Effect of 350 Hours' Exposure at Temperatures Between 200 Degrees Cent. (392 Degrees Fahr.) and 870 Degrees Cent. (1600 Degrees Fahr.) On Impact Toughness of Molybdenum and Columbium-Bearing Chromium-Nickel Steels. The Steels Were Air-Cooled from 1100 Degrees Cent. (2010 Degrees Fahr.) Prior to Exposure to the Holding Temperature.

is insoluble under these conditions in the iron-chromium-nickel solid solution. This means that the austenite-carbide field changes very little when the steels are heated four hours at 870 degrees Cent. (1600 degrees Fahr.); this is important because as will be shown later, neither does corrosion resistance change appreciably if the steel is in

the austenite-carbide field. Other than this, the structures of the steels containing columbium remain substantially the same as those without columbium. The single exception is that the columbium steels contain carbides precipitated at random after annealing at 1100 to 1150 degrees Cent. (2010 to 2100 degrees Fahr.) and are not subject to further serious carbide precipitation. Columbium did eliminate the ill effects of carbide precipitation in the austenite phase,

Table III
Compositions of Steels Used in Izod Impact Tests
(Figs. 13 to 16)

Heat No.	Per Cent						
	Chromium	Nickel	Manganese	Silicon	Molybdenum	Columbium	Carbon
A647	18.85	8.21	0.51	0.28	....	....	0.06
E600	18.30	10.04	1.49	0.47	1.27	....	0.06
E597	18.54	11.78	1.52	0.50	1.78	....	0.05
E501	18.22	12.54	1.60	0.51	2.13	....	0.06
E499	18.19	13.56	1.75	0.57	2.85	....	0.05
E520	18.26	13.98	1.79	0.58	3.62	....	0.05
B140	18.04	8.86	0.54	0.42	....	0.78	0.08
E601	18.18	12.14	1.52	0.51	1.27	0.71	0.07
E599	18.21	12.52	1.51	0.59	1.83	0.54	0.06
E556	18.17	12.80	1.66	0.59	2.07	0.61	0.07
E503	18.10	14.84	1.65	0.67	2.75	0.89	0.06
E504	18.38	16.02	1.63	0.57	3.51	0.83	0.05

but had no stabilizing effect on the secondary constituents (ferrite or sigma) which are the result of the ratio of austenite to ferrite-forming elements in the steel.

Inasmuch as the results of the structural investigation showed that fairly large amounts of sigma were formed in the higher molybdenum content steels (3 per cent or more molybdenum) it was decided to determine the effect of this constituent on the physical characteristics of the steels. It was also decided to make these experiments on steels containing sufficient nickel to render them austenitic after air cooling from 1100 to 1150 degrees Cent. (2010 to 2100 degrees Fahr.), and to test the steels at temperatures of 200, 315, 425, 535, 650, 760 and 870 degrees Cent. (390, 600, 800, 1000, 1200, 1400 and 1600 degrees Fahr.) for periods extending up to several hundred hours to see whether the steels lost toughness under these conditions. Steels containing approximately 1, 2, 2.75, and 3.50 per cent molybdenum with and without columbium were included in these tests, and the results obtained are summarized in Figs. 13 to 16 inclusive. After the samples were held at the indicated temperatures they were air-cooled and tested for toughness at room temperature. The actual compositions of the steels used in the tests are given in Table III.

These data show that all the steels retain their toughness after several hundred hours' exposure at temperatures up to 650 degrees Cent. (1200 degrees Fahr.) but when the molybdenum content is increased beyond 2 per cent the steels suffer a marked decrease in toughness on exposure to temperatures of approximately 760 and 870 degrees Cent. (1400 and 1600 degrees Fahr.). The decrease in toughness after exposure to these two temperatures is quite marked even after a 72-hour holding period, and it is therefore concluded that when much sigma is formed in the higher molybdenum steels, a marked decrease in toughness occurs. The examination of the higher molybdenum content steels under the microscope revealed that their structure contained large quantities of the sigma constituent. This afforded an opportunity to obtain enough of the constituent for identification. After some experimentation, an electrolytic separation of the sigma constituent from a low carbon steel containing about 3.50 per cent molybdenum was made. This separation was made on a sample of the steel held several hundred hours at 870 degrees Cent. (1600 degrees Fahr.) and air cooled. The separation was made in a bath consisting of one part water and one part concentrated hydrochloric acid, using a cell operating under 6 volts with a direct current between 10 and 20 amperes per square inch, the sample being used as the anode in the cell.

The residue obtained from the separation was subjected to an X-ray diffraction test, and the pattern obtained showed strong sigma lines thereby establishing the presence of the sigma phase. The presence of this constituent seems to partly explain some of the difficulties met with in hot working the higher molybdenum content chromium-nickel steels, because it would undoubtedly be formed during hot working as the temperature decreases. The presence of this constituent in the higher molybdenum content steels after heating at 870 degrees Cent. (1600 degrees Fahr.) also shows the inadvisability of stress-relieving these steels even for relatively short periods at this temperature. Thus, in order to avoid this difficulty it is advisable to hold the molybdenum content of steels of the 18-8 type in the neighborhood of 2 per cent, rather than at 2.75 per cent or higher. The 2 per cent molybdenum steels function quite normally in regard to austenite decomposition as there is only a relatively small decrease in toughness on holding at these higher temperatures. The typical appearance of sigma in the high molybdenum content steels is shown in Fig. 16a.

In beginning the investigation of the corrosion resistance of the steels containing different percentages of molybdenum with and without columbium, it was first decided to make a few intergranular corrosion experiments to see how the steels performed. The results of these tests are shown in Table IV.

The solution used in these tests contained 6 per cent by weight of copper sulphate and 16 per cent by weight of sulphuric acid. The 20-gage sheet samples were heated as shown in Table IV, and afterwards exposed to this solution to determine whether they were sub-

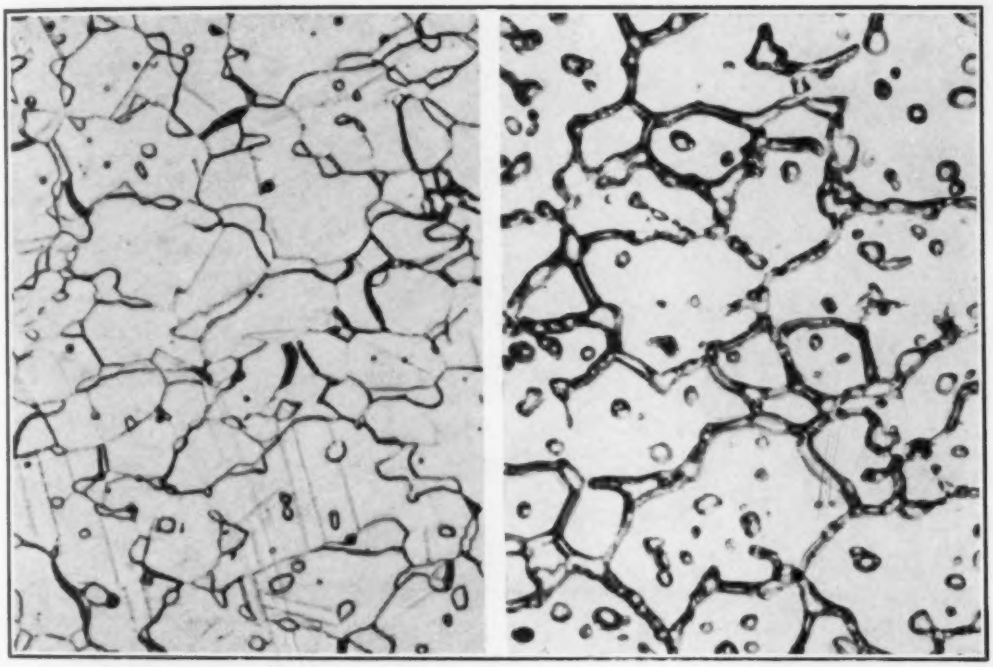

Fig. 16a—Photomicrographs Showing the Etched Structure of a Steel Containing 18.30 Per Cent Chromium, 9.58 Per Cent Nickel, 0.46 Per Cent Manganese, 0.47 Per Cent Silicon, 3.26 Per Cent Molybdenum and 0.06 Per Cent Carbon. × 500.

Left—Heated 10 Minutes at 1100 Degrees Cent. (2010 Degrees Fahr.) and Air-cooled. The Structure of the Steel After This Treatment Consists of Austenite and Ferrite.

Right—Heated 10 Minutes at 1100 Degrees Cent. (2010 Degrees Fahr.) and Air-cooled; Reheated 4 Hour at 870 Degrees Cent. (1600 Degrees Fahr.) and Air-cooled. Practically All of the Ferrite is Converted to Sigma by this Treatment.

ject to grain boundary corrosion. This was determined by bending the samples after exposure to the solution and noting whether the metal cracked badly in the bent section. The results showed that the steels without columbium were subject to intergranular attack.

A large number of the steels were next investigated for resistance to a boiling 65 per cent nitric acid solution. The tests consumed three 48-hour periods, fresh acid being used for each period. The results are reported as the average rate (inch penetration per month). Steels

Table IV
Results of Intergranular Corrosion Tests

Heat No.	Per Cent Chromium	Nickel	Molybdenum	Manganese	Silicon	Columbium	Carbon	Condition of Metal*	Results of Boiling Acidified Copper Sulphate Tests
N79	18.73	10.59	2.56	1.98	0.37	....	0.06	Held 12 hr. at 650° C. (1200° F.) and air cooled.	Disintegrated in 5 hr.
C 5	18.14	13.62	3.19	1.50	0.35	....	0.06	Held 4 hr. at 650° C. (1200° F.) and air cooled.	Disintegrated in 24 hr.
N77	18.31	10.82	2.53	1.66	0.24	0.55	0.06	Held 12 hr. at 650° C. (1200° F.) and air cooled.	Unaffected in 300 hr.
N77	18.31	10.82	2.53	1.66	0.24	0.55	0.06	Held 72 hr. at 650° C. (1200° F.) and air cooled.	Unaffected in 300 hr.
N77	18.31	10.82	2.53	1.66	0.24	0.55	0.06	Held 100 hr. at 650° C. (1200° F.) and air cooled.	Unaffected in 300 hr.
N77	18.31	10.82	2.53	1.66	0.24	0.55	0.06	Held 336 hr. at 650° C. (1200° F.) and air cooled.	Unaffected in 300 hr.
CX	17.87	13.60	2.85	1.50	0.40	0.58	0.06	Held 12 hr. at 650° C. (1200° F.) and air cooled.	Unaffected in 100 hr.

*All samples previously air-cooled from 1150° C. (2100° F.).

of different chromium, nickel, molybdenum, and columbium contents were tested in this acid but for the sake of brevity only the results obtained on the 18 to 19 per cent chromium steels with different percentages of nickel, molybdenum and columbium will be discussed.

Samples of the steels were tested after exposure under four different conditions:

I. Heated 5 to 10 minutes at 1100 to 1150 degrees Cent. (2010 to 2100 degrees Fahr.) and air cooled.

II. Heated 5 to 10 minutes at 1100 to 1150 degrees Cent. (2010 to 2100 degrees Fahr.) and air cooled; reheated 4 hr. at 870 degrees Cent. (1600 degrees Fahr.) and air cooled.

III. Heated 5 to 10 minutes at 1100 to 1150 degrees Cent. (2010 to 2100 degrees Fahr.) and air cooled; reheated 4 hr. at 870 degrees Cent. (1600 degrees Fahr.) and air cooled; reheated 4 hr. at 650 degrees Cent. (1200 degrees Fahr.) and air cooled.

IV. Heated 5 to 10 minutes at 1100 to 1150 degrees Cent. (2010 to 2100 degrees Fahr.) and air cooled; reheated 4 hr. at 650 degrees Cent. (1200 degrees Fahr.) and air cooled.

These four different heat treatments were applied to steels, with and without columbium additions, and the results obtained are given in Tables V and VI. Table V shows the results obtained on polished samples of the chromium-nickel steels containing molybdenum after the different heat treatments. Table VI shows the results of similar tests on the molybdenum-bearing steels containing between nine and fourteen times as much columbium as carbon.

These data reveal the importance of adding sufficient nickel to the annealed steels of different molybdenum contents to obtain a substantially austenitic structure, which assures optimum resistance to the boiling nitric acid solution. The effect of nickel on corrosion resistance is also brought out in the tests on the samples heated respectively at 870 and 650 degrees Cent. (1600 and 1200 degrees Fahr.). In these two instances when the nickel content was too low in accordance with the previously discussed structural diagrams, the losses in nitric acid were extremely high. Therefore, these data clearly show the necessity of balancing the compositions of the steels in order to obtain the highest degree of corrosion resistance.

In order to make plain the effects of molybdenum alone on the corrosion resistance of the steels, data were obtained on fully austenitic steels containing approximately 1, 2, and 3 per cent molybde-

Table V
Corrosion Tests in Boiling 65 Per Cent Nitric Acid

Heat No.	Per Cent						Average Corrosion Rate, Inch Penetration Per Month			
	Chromium	Nickel	Molybdenum	Manganese	Silicon	Carbon	Heated 5 Min. at 1100-1150° C. and A.C.†	Heated 5 Min. at 1100-1150° C. and A.C., Reheated 4 Hr. at 870° C. and A.C.	Heated 5 Min. at 1100-1150° C. and A.C., Reheated 4 Hr. at 650° C. and A.C.	Heated 5 Min. at 1100-1150° C. and A.C., Reheated 4 Hr. at 650° C. and A.C.
E236	17.94	11.83	1.20	1.54	0.45	0.08	0.00077	0.00320	0.0217	0.0267
E 69	18.25	12.09	1.29	1.55	0.50	0.08	0.00064	0.00420	0.0325	0.0580
E456	18.04	11.89	1.59	1.57	0.44	0.07	0.00056	0.00197	0.0170	0.0388
B927	18.20	8.72	2.20	0.56	0.53	0.10	0.00114	.....	0.0123	0.1010
C921	18.13	9.16	2.61	0.45	0.47	0.06	0.00110	0.00181	0.0138*	0.0639*
N 79	18.73	10.59	2.56	1.98	0.37	0.06	0.00077	0.00096	0.0036*	0.0290*
E612	17.86	11.85	2.03	1.66	0.50	0.07	0.00087	0.00173	0.0064	0.0252
D821	18.02	13.75	2.18	1.52	0.51	0.07	0.00070	0.00267	0.0087	0.0315
E397	18.13	13.75	2.07	1.59	0.44	0.06	0.00063	0.00080	0.0039	0.0232
E457	17.93	13.83	2.00	1.62	0.45	0.07	0.00064	0.00254	0.0173	0.0461
D822	18.08	13.89	2.59	1.48	0.47	0.07	0.00073	0.00190	0.0074	0.0255
E613	18.02	15.95	2.06	1.63	0.49	0.05	0.00061	0.00101	0.0022	0.0185
E418	20.60	16.15	2.47	1.69	0.44	0.06	0.00063	0.00091	0.0035	0.0369
C922	18.30	9.58	3.26	0.46	0.47	0.05	0.00700	0.00117	0.0033*	0.1480*
E614	17.90	10.18	3.27	1.61	0.49	0.07	0.00136	0.00293	0.0143	0.1150
C920	17.76	10.48	3.23	0.47	0.48	0.08	0.00100	0.00497	0.0302*	0.0500*
E615	18.14	11.66	3.17	1.68	0.48	0.05	0.00103	0.00150	0.0037	0.0900
D823	17.95	13.80	2.96	1.56	0.56	0.08	0.00100	0.00670	0.0293	0.0446
{Type 317	17.92	13.61	3.30	1.87	0.37	0.06	0.00084	0.00279	0.0390	0.0660
E402	18.13	14.91	3.48	1.63	0.50	0.08	0.00114	0.00535	0.0348	0.0490
E413	18.20	14.76	3.37	1.63	0.42	0.06	0.00103	0.00315	0.0315	0.0423
E471	18.18	17.97	3.59	1.65	0.42	0.05	0.00086	0.00213	0.0260	0.0429

*2 hr. at 650° C. †Air-cooled.

Table VI
Corrosion Tests in Boiling 65 Per Cent Nitric Acid

Heat No.	Per Cent							Average Corrosion Rate, Inch Penetration Per Month			
	Chromium	Nickel	Molybdenum	Manganese	Silicon	Columbium	Carbon	Heated 5 Min. at 1100-1150° C. and A.C.*	Heated 5 Min. at 1100-1150° C. and A.C., Reheated 4 Hr. at 870° C. and A.C.	Heated 5 Min. at 1100-1150° C. and A.C., Reheated 4 Hr. at 870° C. and A.C., Reheated 4 Hr. at 650° C. and A.C.	Heated 5 Min. at 1100-1150° C. and A.C., Reheated 4 Hr. at 650° C. and A.C.
E404	18.25	10.40	1.53	1.69	0.54	0.72	0.07	0.00069	0.00074	0.00089	0.0033
D646	18.36	12.01	1.60	1.55	0.32	0.56	0.06	0.00097	0.00132	0.00150	0.0030
E312	18.03	12.11	1.63	1.60	0.46	0.78	0.05	0.00068	0.00074	0.00087	0.0018
E405	18.22	14.00	1.52	1.64	0.52	0.72	0.07	0.00063	0.00062	0.00074	0.0015
D649	18.33	18.05	1.57	1.48	0.40	0.56	0.08	0.00109	0.00177	0.00775	0.0800
D325	18.14	10.03	2.03	1.54	0.35	0.77	0.08	0.00176	0.00216	0.00312	0.0280
E309	17.90	12.04	1.99	1.54	0.45	0.87	0.06	0.00081	0.00087	0.00121	0.0082
E408	18.23	12.47	2.01	1.69	0.55	0.76	0.08	0.00075	0.00076	0.00133	0.0091
E416	18.40	12.51	2.00	1.64	0.48	0.69	0.06	0.00073	0.00071	0.00094	0.0018
E275	17.79	12.95	2.02	1.52	0.66	0.95	0.07	0.00080	0.00081	0.00108	0.0014
E409	18.21	13.42	2.02	1.65	0.53	0.75	0.07	0.00073	0.00071	0.00113	0.0035
E478	18.31	13.48	2.04	1.72	0.56	0.75	0.06	0.00060	0.00062	0.00079	0.0022
D327	17.73	13.85	2.04	1.52	0.42	0.74	0.07	0.00070	0.00180	0.00269	0.0040
D328	17.91	15.82	2.06	1.53	0.39	0.77	0.06	0.00080	0.00201	0.00337	0.0065
E415	18.45	18.11	2.02	1.50	0.50	0.75	0.06	0.00072	0.00065	0.00106	0.0034
E407	18.37	18.01	2.02	1.63	0.53	0.76	0.08	0.00070	0.00066	0.00162	0.0093

*Air-cooled.

Table VI—(Continued)

Heat No.	Per Cent							Average Corrosion Rate, Inch Penetration Per Month			
	Chromium	Nickel	Molybdenum	Manganese	Silicon	Columbium	Carbon	Heated 5 Min. at 1100-1150° C. and A.C.*	Heated 5 Min. at 1100-1150° C. and A.C., Reheated 4 Hr. at 870° C. and A.C.	Heated 5 Min. at 1100-1150° C. and A.C., Reheated 4 Hr. at 870° C. and A.C., Reheated 4 Hr. at 650° C. and A.C.	Heated 5 Min. at 1100-1150° C. and A.C., Reheated 4 Hr. at 650° C. and A.C.
D320	18.54	9.92	2.64	1.47	0.53	0.76	0.06	0.00316	0.00238	0.00332	0.0635
E310	18.22	11.91	2.70	1.60	0.52	0.81	0.06	0.00158	0.00130	0.00566	0.0549
D321	18.65	12.26	2.71	1.48	0.60	0.82	0.07	0.00206	0.00272	0.00376	0.0154
D900	18.22	12.67	2.79	2.13	0.45	0.54	0.06	0.00099	0.00107	0.00173	0.0176
D322	17.96	13.68	2.61	1.52	0.53	0.78	0.06	0.00126	0.00215	0.00264	0.0043
E276	18.30	13.79	2.42	1.56	0.67	0.91	0.07	0.00105	0.00108	0.00128	0.0048
E414	18.20	15.93	2.48	1.56	0.49	0.70	0.05	0.00072	0.00063	0.00090	0.0019
E406	18.28	16.05	2.56	1.61	0.53	0.75	0.08	0.00085	0.00096	0.00282	0.0112
D324	18.42	17.99	2.69	1.57	0.52	0.73	0.07	0.00155	0.00192	0.00361	0.0078
D329	17.85	10.51	3.02	1.52	0.46	0.76	0.06	0.03610	0.00290	0.00428	0.1860
D330	17.91	11.87	3.09	1.49	0.48	0.68	0.07	0.00362	0.00299	0.00404	0.0390
D331	17.97	13.85	3.19	1.46	0.40	0.75	0.07	0.00227	0.00303	0.00417	0.0106
D332	17.68	15.78	3.19	1.51	0.46	0.73	0.06	0.00110	0.00150	0.00436	0.0050
D921	18.15	16.02	3.47	2.16	0.52	0.59	0.06	0.00169	0.00132	0.00918	0.0303
D333	18.01	17.91	3.01	1.48	0.52	0.76	0.03	0.00183	0.00275	0.00324	0.0113
E410	18.51	17.93	3.50	1.64	0.59	0.76	0.08	0.00145	0.00139	0.00297	0.0210
E417	18.20	17.88	3.45	1.70	0.51	0.75	0.07	0.00120	0.00128	0.00229	0.0158

*Air-cooled.

num, with and without columbium, and have been plotted in Figs. 17, 18, and 19. The actual data used in constructing these curves are given in Tables VII, VIII, and IX. These figures also relate to

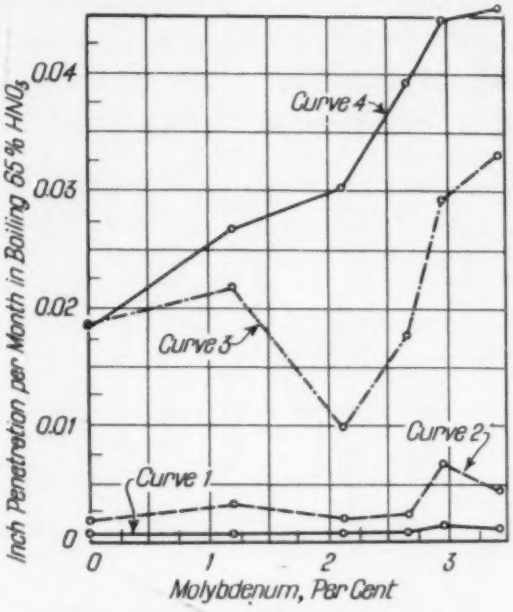

Fig. 17 — Curves Showing Effect of Heat Treatment on Corrosion Resistance of Molybdenum-Bearing Steels in Boiling 65 Per Cent Nitric Acid.

Curve 1—Heated 5 Minutes at 1100 to 1150 Degrees Cent. (2010 to 2100 Degrees Fahr.) and Air-Cooled.

Curve 2—Heated 5 Minutes at 1100 to 1150 Degrees Cent. (2010 to 2100 Degrees Fahr.) and Air-Cooled; Reheated 4 Hours at 870 Degrees Cent. (1600 Degrees Fahr.) and Air-Cooled.

Curve 3—Heated 5 Minutes at 1100 to 1150 Degrees Cent. (2010 to 2100 Degrees Fahr.) and Air-Cooled; Reheated 4 Hours at 870 Degrees Cent. (1600 Degrees Fahr.) and Air-Cooled; Reheated 4 Hours at 650 Degrees Cent. (1200 Degrees Fahr.) and Air-Cooled.

Curve 4—Heated 5 Minutes at 1100 to 1150 Degrees Cent. (2010 to 2100 Degrees Fahr.) and Air-Cooled; Reheated 4 Hours at 650 Degrees Cent. (1200 Degrees Fahr.) and Air-Cooled.

the different heat treatments applied to the steels. As shown in Fig. 17, the corrosion resistance of the annealed chromium-nickel steels containing various amounts of molybdenum does not materially change as the molybdenum content is increased from somewhat over 1 to somewhat over 3 per cent but when the annealed steels are heated at 870 degrees Cent. (1600 degrees Fahr.) or 650 degrees Cent. (1200 degrees Fahr.) they suffer a lowering of corrosion resistance, which decreases as the molybdenum content exceeds 3 per cent. This

undoubtedly means that the sigma constituent and precipitated carbides in the steels produce a lowering of corrosion resistance to oxidizing media. The data also indicate that if the molybdenum-bearing chromium-nickel steels are stress-relieved at 870 degrees Cent. (1600 degrees Fahr.) maximum corrosion resistance is not retained.

The data of Fig. 17 and Table V are especially pertinent in connection with the effect of sigma on corrosion resistance. These data

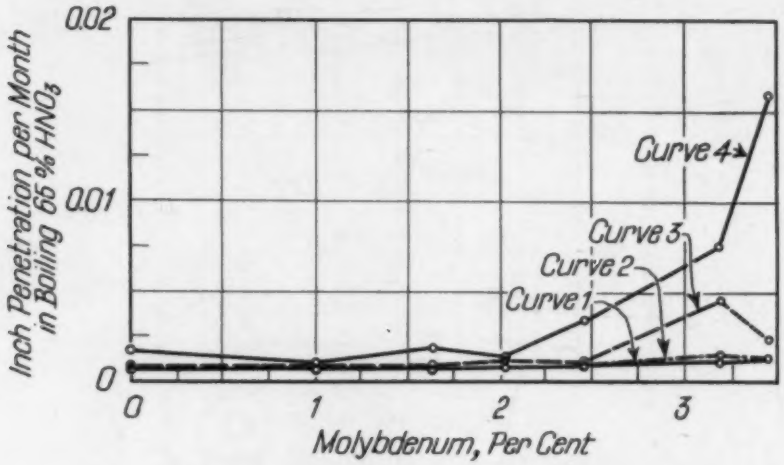

Fig. 18—Curves Showing Effect of Heat Treatment on Corrosion Resistance of Molybdenum-Bearing Steels Containing Ten to Fifteen Times as Much Columbium as Carbon in Boiling 65 Per Cent Nitric Acid.

Curve 1—Heated 5 Minutes at 1100 to 1150 Degrees Cent. (2010 to 2100 Degrees Fahr.) and Air-Cooled.

Curve 2—Heated 5 Minutes at 1100 to 1150 Degrees Cent. (2010 to 2100 Degrees Fahr.) and Air-Cooled; Reheated 4 Hours at 870 Degrees Cent. (1600 Degrees Fahr.) and Air-Cooled.

Curve 3—Heated 5 Minutes at 1100 to 1150 Degrees Cent. (2010 to 2100 Degrees Fahr.) and Air-Cooled; Reheated 4 Hours at 870 Degrees Cent. (1600 Degrees Fahr.) and Air-Cooled; Reheated 4 Hours at 650 Degrees Cent. (1200 Degrees Fahr.) and Air-Cooled.

Curve 4—Heated 5 Minutes at 1100 to 1150 Degrees Cent. (2010 to 2100 Degrees Fahr.) and Air-Cooled; Reheated 4 Hours at 650 Degrees Cent. (1200 Degrees Fahr.) and Air-Cooled.

show, that even though the greatest loss in toughness due to sigma formation occurs as previously described on heating at 870 degrees Cent. (1600 degrees Fahr.), the highest loss in corrosion resistance to oxidizing media results from heating at 650 degrees Cent. (1200 degrees Fahr.) at which temperature the loss in toughness is relatively slight. This might give the impression that sigma produces little adverse effect on corrosion resistance unless it is realized that the phase is also formed on holding at 650 degrees Cent. (1200 degrees Fahr.). The greater corrosion loss resulting from exposure to 650 degrees Cent. (1200 degrees Fahr.) is probably due to the fact that the precipitated carbides and the sigma phase are in a finely

divided state which produces a greater adverse effect on corrosion resistance than the larger carbide and sigma phase particles formed on heating at 870 degrees Cent. (1600 degrees Fahr.).

The data of Figs. 18 and 19 were obtained on steels of similar molybdenum contents that contained columbium. The columbium-bearing steels, particularly those containing at least nine times as much columbium as carbon, retained their corrosion resistance after

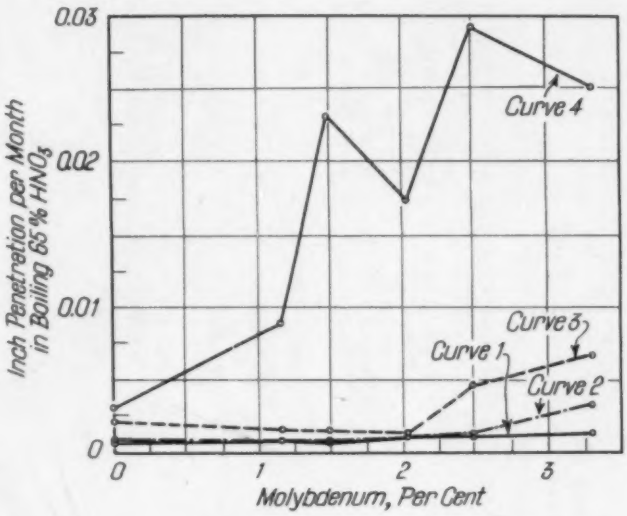

Fig. 19—Curves Showing Effect of Heat Treatment on Corrosion Resistance of Molybdenum-Bearing Steels Containing Six to Eight Times as Much Columbium as Carbon, in Boiling 65 Per Cent Nitric Acid.

Curve 1—Heated 5 Minutes at 1100 to 1150 Degrees Cent. (2010 to 2100 Degrees Fahr.) and Air-Cooled.

Curve 2—Heated 5 Minutes at 1100 to 1150 Degrees Cent. (2010 to 2100 Degrees Fahr.) and Air-Cooled; Reheated 4 Hours at 870 Degrees Cent. (1600 Degrees Fahr.) and Air-Cooled.

Curve 3—Heated 5 Minutes at 1100 to 1150 Degrees Cent. (2010 to 2100 Degrees Fahr.) and Air-Cooled; Reheated 4 Hours at 870 Degrees Cent. (1600 Degrees Fahr.) and Air-Cooled; Reheated 4 Hours at 650 Degrees Cent. (1200 Degrees Fahr.) and Air-Cooled.

Curve 4—Heated 5 Minutes at 1100 to 1150 Degrees Cent. (2010 to 2100 Degrees Fahr.) and Air-Cooled; Reheated 4 Hours at 650 Degrees Cent. (1200 Degrees Fahr.) and Air-Cooled.

heating under similar conditions provided their molybdenum content did not greatly exceed about 2 per cent. However, if the molybdenum content extended to 3 per cent and higher these steels also suffered a decrease in corrosion resistance after heating at 870 degrees Cent. (1600 degrees Fahr.) and 650 degrees Cent. (1200 degrees Fahr.) which shows that the sigma constituent has an adverse effect on this property. Referring again to the 2 per cent molybdenum

Table VII
Nitric Acid Corrosion Data Corresponding to Fig. 17

Heat No.	Per Cent Chromium	Nickel	Molybdenum	Manganese	Silicon	Carbon	Average Corrosion Rate, Inch Penetration Per Month: Heated 5 Min. at 1100-1150° C. and A.C.*	Heated 5 Min. at 1100-1150° C. and A.C., Reheated 4 Hr. at 870° C. and A.C.	Heated 5 Min. at 1100-1150° C. and A.C., Reheated 4 Hr. at 650° C. and A.C.	Heated 5 Min. at 1100-1150° C. and A.C., Reheated 4 Hr. at 650° C. and A.C.
Type 304	18.65	9.70	....	0.47	0.32	0.08				
Type 306	18.25	9.70	....	0.55	0.44	0.06	0.00070	0.0019	0.0186	0.0183
47470	18.80	8.60	....	0.46	0.40	0.06				
E236	17.94	11.83	1.20	1.54	0.45	0.08	0.00077	0.0032	0.0217	0.0267
E397	18.13	13.75	2.07	1.59	0.44	0.06				
D821	18.02	13.75	2.18	1.52	0.51	0.07	0.00079	0.0020	0.0098	0.0303
E457	17.93	13.83	2.00	1.62	0.45	0.07				
D822	18.08	13.89	2.59	1.48	0.47	0.07				
Type 316	17.74	13.77	2.74	1.67	0.35	0.07	0.00091	0.0024	0.0177	0.0392
D823	17.95	13.80	2.96	1.56	0.56	0.08	0.00139	0.0067	0.0293	0.0446
E402	18.13	14.91	3.48	1.63	0.50	0.08				
E413	18.20	14.76	3.37	1.63	0.42	0.06	0.00110	0.0043	0.0332	0.0457

*Air-cooled.

Table VIII
Nitric Acid Corrosion Data Corresponding to Fig. 18

Heat No.	Per Cent Chromium	Nickel	Molybdenum	Columbium	Manganese	Silicon	Carbon	Average Corrosion Rate, Inch Penetration Per Month: Heated 5 Min. at 1100-1150° C. and A.C.*	Heated 5 Min. at 1100-1150° C. and A.C., Reheated 4 Hr. at 870° C. and A.C.	Heated 5 Min. at 1100-1150° C. and A.C., Reheated 4 Hr. at 870° C. and A.C., Reheated 4 Hr. at 650° C. and A.C.	Heated 5 Min. at 1100-1150° C. and A.C., Reheated 4 Hr. at 650° C. and A.C.
N86	18.86	9.45	....	0.75	0.65	0.49	0.06				
18-8C	18.77	11.57	....	0.97	1.80	0.45	0.05				
Type 347	17.59	11.48	....	0.76	1.86	1.00	0.07	0.00069	0.00068	0.00082	0.00168
E274	18.41	10.94	0.99	0.89	1.52	0.61	0.07	0.00071	0.00073	0.00081	0.00097
E312	18.03	12.11	1.63	0.78	1.60	0.46	0.05	0.00068	0.00074	0.00087	0.00179
E275	17.79	12.95	2.02	0.95	1.52	0.66	0.07	0.00080	0.00081	0.00108	0.00140
E414	18.20	15.93	2.48	0.70	1.56	0.49	0.05				
E276	18.30	13.79	2.42	0.91	1.56	0.67	0.07	0.00089	0.00086	0.00109	0.00334
D332	17.68	15.78	3.19	0.73	1.51	0.46	0.06	0.00110	0.00150	0.00440	0.00750
E417	18.20	17.88	3.45	0.75	1.70	0.51	0.07	0.00120	0.00128	0.00229	0.01580

*Air-cooled.

Table IX
Nitric Acid Corrosion Data Corresponding to Fig. 19

Heat No.	Per Cent							Average Corrosion Rate, Inch Penetration Per Month			
	Chromium	Nickel	Molybdenum	Columbium	Manganese	Silicon	Carbon	Heated 5 Min. at 1100-1150° C. and A.C.*	Heated 5 Min. at 1100-1150° C. and A.C., Reheated 4 Hr. at 870° C. and A.C.	Heated 5 Min. at 1100-1150° C. and A.C., Reheated 4 Hr. at 870° C. and A.C., Reheated 4 Hr. at 650° C. and A.C.	Heated 5 Min. at 1100-1150° C. and A.C., Reheated 4 Hr. at 650° C. and A.C.
N 87	17.65	9.85	....	0.34	0.97	0.42	0.05	0.00066	0.00090	0.00220	0.0031
E237	18.46	11.99	1.16	0.49	1.59	0.52	0.06	0.00080	0.00090	0.00158	0.0089
E243	18.48	11.74	1.49	0.48	1.54	0.57	0.07	0.00070	0.00080	0.00150	0.0231
D657	18.40	11.76	2.03	0.40	1.56	0.33	0.07	0.00110	0.00107	0.00140	0.0174
D660	18.28	13.82	2.49	0.42	1.52	0.31	0.07	0.00122	0.00144	0.00456	0.0291
E238	18.74	16.09	3.31	0.50	2.18	0.49	0.07	0.00137	0.00344	0.00670	0.0250

*Air-cooled.

steels, the results show that if the columbium content is six times the carbon content these steels can be heated at the stress-relieving temperature of 870 degrees Cent. (1600 degrees Fahr.) after annealing, without suffering a marked loss in corrosion resistance. It can be concluded that if the molybdenum content is maintained at about

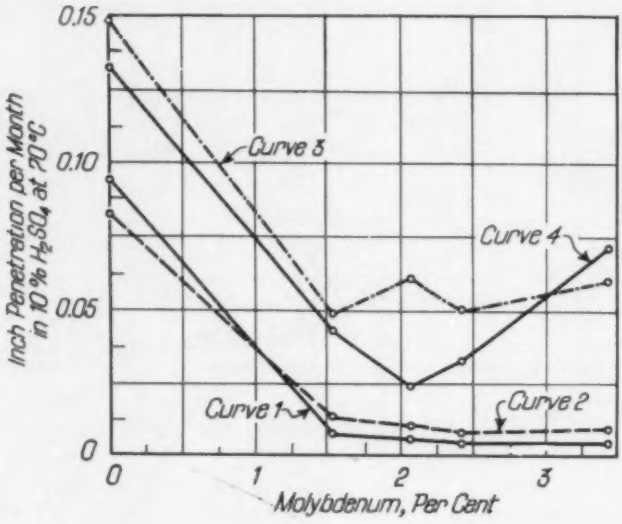

Fig. 20—Curves Showing Effect of Heat Treatment on Corrosion Resistance of Molybdenum-Bearing Steels in 10 Per Cent Sulphuric Acid at 70 Degrees Cent.

Curve 1—Heated 5 Minutes at 1100 to 1150 Degrees Cent. (2010 to 2100 Degrees Fahr.) and Air-Cooled.

Curve 2—Heated 5 Minutes at 1100 to 1150 Degrees Cent. (2010 to 2100 Degrees Fahr.) and Air-Cooled; Reheated 4 Hours at 870 Degrees Cent. (1600 Degrees Fahr.) and Air-Cooled.

Curve 3—Heated 5 Minutes at 1100 to 1150 Degrees Cent. (2010 to 2100 Degrees Fahr.) and Air-Cooled; Reheated 4 Hours at 870 Degrees Cent. (1600 Degrees Fahr.) and Air-Cooled; Reheated 4 Hours at 650 Degrees Cent. (1200 Degrees Fahr.) and Air-Cooled.

Curve 4—Heated 5 Minutes at 1100 to 1150 Degrees Cent. (2010 to 2100 Degrees Fahr.) and Air-Cooled; Reheated 4 Hours at 650 Degrees Cent. (1200 Degrees Fahr.) and Air-Cooled.

2 per cent in a substantially austenitic type of chromium-nickel steel a marked improvement is obtained by the columbium addition. These steels will retain their corrosion resistance after heating at the stress-relieving temperatures, which renders them far more suitable for use under conditions requiring stress-relieving after fabrication.

After obtaining the foregoing data in boiling 65 per cent nitric acid, it was decided to test the same steels in acids of a reducing instead of an oxidizing nature. Sulphuric acid solutions and acetic

acid vapors and condensate were selected for this purpose. The tests in sulphuric acid were made in a solution containing 10 per cent by weight of this acid and the solution was heated to 70 degrees Cent. (160 degrees Fahr.). The samples were completely immersed in the sulphuric acid solution and the test was conducted using a nitro-

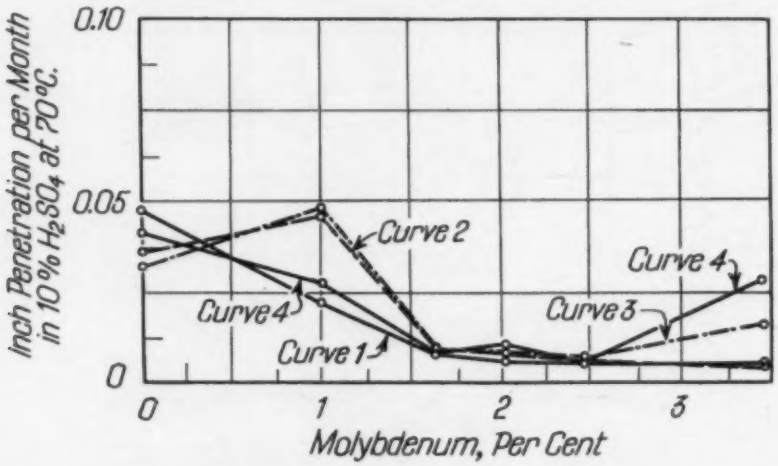

Fig. 21—Curves Showing Effect of Heat Treatment on Corrosion Resistance of Molybdenum-Bearing Steels Containing Ten to Fifteen Times as Much Columbium as Carbon in 10 Per Cent Sulphuric Acid at 70 Degrees Cent.

Curve 1—Heated 5 Minutes at 1100 to 1150 Degrees Cent. (2010 to 2100 Degrees Fahr.) and Air-Cooled.

Curve 2—Heated 5 Minutes at 1100 to 1150 Degrees Cent. (2010 to 2100 Degrees Fahr.) and Air-Cooled; Reheated 4 Hours at 870 Degrees Cent. (1600 Degrees Fahr.) and Air-Cooled.

Curve 3—Heated 5 Minutes at 1100 to 1150 Degrees Cent. (2010 to 2100 Degrees Fahr.) and Air-Cooled; Reheated 4 Hours at 870 Degrees Cent. (1600 Degrees Fahr.) and Air-Cooled; Reheated 4 Hours at 650 Degrees Cent. (1200 Degrees Fahr.) and Air-Cooled.

Curve 4—Heated 5 Minutes at 1100 to 1150 Degrees Cent. (2010 to 2100 Degrees Fahr.) and Air-Cooled; Reheated 4 Hours at 650 Degrees Cent. (1200 Degrees Fahr.) and Air-Cooled.

gen atmosphere, so as to eliminate inconsistencies in test results. After the samples were immersed and the sulphuric acid solution brought to temperature, the samples were touched with a small iron wire to start a reaction. The results obtained in these experiments made on steels similar to those previously tested in the boiling nitric acid, are given in Figs. 20 and 21, and Tables X and XI.

The losses obtained in the 10 per cent sulphuric acid test were considerably higher than those suffered by the steels during exposure to nitric acid. The most important observation made in the sulphuric tests was that molybdenum additions were very effective in improving the resistance of the steels to this acid. For example, it is shown in Fig. 20 that with as little as about 1.50 per cent molybdenum the

Table X

Sulphuric Acid Corrosion Data Coresponding to Fig. 20

Heat No.	Per Cent Chromium	Nickel	Molybdenum	Manganese	Silicon	Carbon	Average Corrosion Rate, Inch Penetration Per Month: Heated 5 Min. at 1100-1150° C. and A.C.*	Heated 5 Min. at 1100-1150° C. and A.C., Reheated 4 Hr. at 870° C. and A.C.	Heated 5 Min. at 1100-1150° C. and A.C., Reheated 4 Hr. at 650° C. and A.C.	Heated 5 Min. at 1100-1150° C. and A.C., Reheated 4 Hr. at 650° C. and A.C.
47470	18.80	8.60	....	0.46	0.40	0.06	0.0940	0.0840	0.1480	0.1320
E396	18.22	12.03	1.53	1.66	0.44	0.05	0.0068	0.0133	0.0490	0.0428
E397	18.13	13.75	2.07	1.59	0.44	0.06	0.0053	0.0102	0.0605	0.0239
E398	18.07	13.91	2.42	1.58	0.50	0.05	0.0046	0.0078	0.0500	0.0331
E413	18.20	14.76	3.37	1.63	0.42	0.06	0.0046	0.0089	0.0601	0.0706
E402	18.13	14.91	3.48	1.63	0.50	0.08				

*Air-cooled.

Table XI

Sulphuric Acid Corrosion Data Corresponding to Fig. 21

Heat No.	Per Cent Chromium	Nickel	Molybdenum	Columbium	Manganese	Silicon	Carbon	Average Corrosion Rate, Inch Penetration Per Month: Heated 5 Min. at 1100-1150° C. and A.C.*	Heated 5 Min. at 1100-1150° C. and A.C., Reheated 4 Hr. at 870° C. and A.C.	Heated 5 Min. at 1100-1150° C. and A.C., Reheated 4 Hr. at 650° C. and A.C.	Heated 5 Min. at 1100-1150° C. and A.C., Reheated 4 Hr. at 650° C. and A.C.
N 86	18.86	9.45	....	0.75	0.65	0.49	0.06	0.0470	0.0357	0.0320	0.0410
E274	18.41	10.94	0.99	0.89	1.52	0.61	0.07	0.0224	0.0460	0.0483	0.0274
E312	18.03	12.11	1.63	0.78	1.60	0.46	0.05	0.0078	0.0091	0.0096	0.0082
E275	17.79	12.95	2.02	0.95	1.52	0.66	0.07	0.0056	0.0078	0.0079	0.0106
E409	18.21	13.42	2.02	0.75	1.65	0.53	0.07				
E414	18.20	15.93	2.48	0.70	1.56	0.49	0.05	0.0053	0.0065	0.0069	0.0058
E276	18.30	13.79	2.43	0.91	1.56	0.67	0.07				
E417	18.20	17.88	3.45	0.75	1.70	0.51	0.07	0.0053	0.0045	0.0159	0.0281
D921	18.15	16.02	3.47	0.59	2.16	0.52	0.06				

*Air-cooled.

resistance of the annealed steels to the sulphuric acid was greatly improved, whereas increasing the molybdenum content to approximately 2 per cent gave steels with almost maximum resistance to this type of corrosion. Heating the molybdenum-bearing steels at 870 degrees Cent. (1600 degrees Fahr.) and 650 degrees Cent. (1200 degrees Fahr.) produced a lowering in resistance to corrosion be-

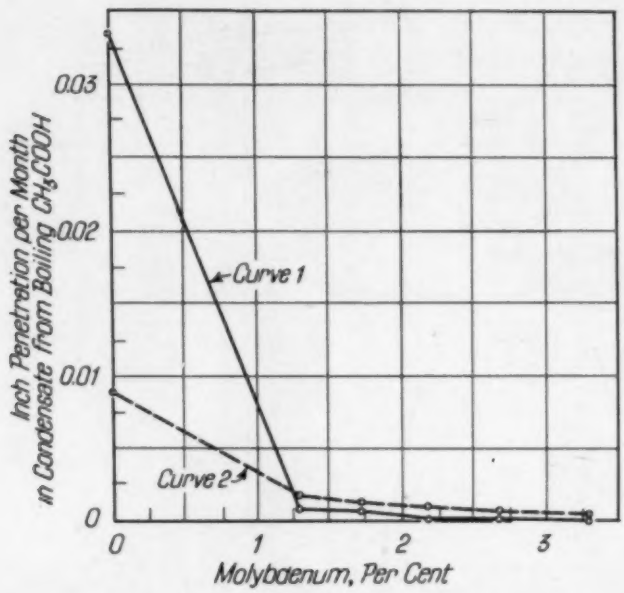

Fig. 22—Curves Showing Effect of Molybdenum on Corrosion Resistance of Chromium-Nickel Steels in Condensate from Boiling Acetic Acid.

Curve 1—Heated 5 Minutes at 1100 to 1150 Degrees Cent. (2010 to 2100 Degrees Fahr.) and Air-Cooled. Tests Conducted in Condensate from Boiling 80 Per Cent Acetic Acid.

Curve 2—Heated 5 Minutes at 1100 to 1150 Degrees Cent. (2010 to 2100 Degrees Fahr.) and Air-Cooled. Tests Conducted in Condensate from Boiling 96 Per Cent Acetic Acid.

cause of carbide precipitation. The steels containing between about 1.50 and slightly over 2 per cent molybdenum suffered the least decrease in corrosion resistance, which again indicates that the sigma phase also lowers corrosion resistance.

The data of Fig. 21 represent the results obtained on similar molybdenum-bearing steels containing columbium. The columbium addition improved the resistance of the steels with different molybdenum contents to the 10 per cent sulphuric acid solution, and as before, maximum resistance to the sulphuric acid was obtained when approximately 2 per cent molybdenum was present. It is pertinent

that the resistance of the 1.5 to 2 per cent molybdenum steel to corrosion by the sulphuric acid solution was maintained almost unimpaired after heating at 870 and 650 degrees Cent. (1600 and 1200 degrees Fahr.). These results on the steels containing columbium will be obtained only if the steels are balanced in regard to their chromium and nickel contents. These data again reveal that if columbium additions are made to the chromium-nickel steels containing no more than approximately 2 per cent molybdenum the steels can be stress-relieved without suffering a serious loss in resistance to the 10 per cent sulphuric acid solution.

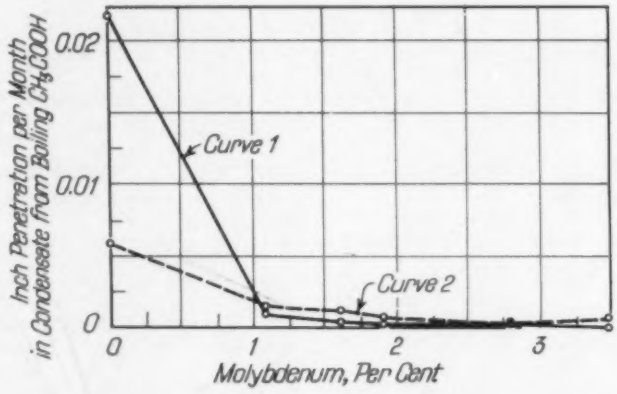

Fig. 23—Curves Showing Effect of Molybdenum on Corrosion Resistance of Columbium-Bearing Chromium-Nickel Steels Containing Seven to Ten Times as Much Columbium as Carbon in Condensate from Boiling Acetic Acid.

Curve 1—Heated 5 Minutes at 1100 to 1150 Degrees Cent. (2010 to 2100 Degrees Fahr.) and Air-Cooled. Tests Conducted in Condensate from Boiling 80 Per Cent Acetic Acid.

Curve 2—Heated 5 Minutes at 1100 to 1150 Degrees Cent. (2010 to 2100 Degrees Fahr.) and Air-Cooled. Tests Conducted in Condensate from Boiling 96 Per Cent Acetic Acid.

The tests in acetic acid were made to obtain data on the effect of molybdenum on the resistance of the annealed steels to this acid. The samples were exposed to the condensates to simulate the worst conditions and the results are given in Tables XII and XIII, and plotted in Figs. 22 and 23.

It is apparent from these data that, as in the case of sulphuric acid, molybdenum additions are extremely effective in reducing the corrosive effect of acetic acid. With the addition of slightly over 1 per cent molybdenum a marked improvement is obtained, and when 2 per cent molybdenum is present the enhancement in regard to at-

tack by acetic acid is practically the same as with somewhat higher molybdenum contents. The addition of columbium to the steels of the various molybdenum contents did not materially change these results.

Practically all of the samples made during this investigation were tested for resistance to pitting and contact corrosion. The samples were tested in the salt spray atmosphere from a 20 per cent sodium chloride solution; were fully immersed in a 4 per cent sodium chloride solution at room temperature, and fully immersed in 10 per cent sodium chloride solutions containing respectively 0.50 and 5 per cent

Table XII
Acetic Acid Corrosion Data Corresponding to Fig. 22

Heat No.	Per Cent Chromium	Nickel	Molybdenum	Manganese	Silicon	Carbon	Average Corrosion Rate—Inch Penetration Per Month: Heated 5 Min. at 1100-1150° C. and Air Cooled Condensate from Boiling 80% Acetic Acid	Heated 5 Min. at 1100-1150° C. and Air Cooled Condensate from Boiling 96% Acetic Acid
D949	18.04	9.69	....	2.02	0.39	0.08	0.0334	0.0089
E 69	18.25	12.09	1.29	1.55	0.50	0.08	0.0008	0.00175
D820	18.04	13.73	1.72	1.48	0.48	0.06	0.00067	0.00131
D821	18.02	13.75	2.18	1.52	0.51	0.07	0.00016	0.00097
Type 316	16.75	12.35	2.67	0.27	0.18	0.08	0.00022	0.00071
Type 317	17.92	13.61	3.30	1.87	0.37	0.06	0.000021	0.00052

Table XIII
Acetic Acid Corrosion Data Corresponding to Fig. 23

Heat No.	Per Cent Chromium	Nickel	Molybdenum	Columbium	Manganese	Silicon	Carbon	Average Corrosion Rate—Inch Penetration Per Month: Heated 5 Min. at 1100-1150° C. and Air Cooled Condensate from Boiling 80% Acetic Acid	Heated 5 Min. at 1100-1150° C. and Air Cooled Condensate from Boiling 96% Acetic Acid
D757	18.54	10.07	....	0.70	2.16	0.53	0.07	0.0217	0.0059
E 74	17.97	11.89	1.08	0.56	1.50	0.48	0.08	0.00085	0.00145
D646	18.36	12.01	1.60	0.56	1.55	0.32	0.06	0.00042	0.00116
D895	18.70	13.00	1.91	0.56	1.95	0.39	0.08	0.00030	0.00072
D900	18.22	12.67	2.79	0.54	2.13	0.45	0.06	0.00027	0.00038
D921	18.15	16.02	3.47	0.59	2.16	0.52	0.06	0.000038	0.00064

ferric chloride at room temperature. It is impractical to give the results of all of these experiments, and a discussion of the data obtained in the sodium chloride solutions containing ferric chloride will suffice. In this instance however, the chromium and molybdenum contents were found to be important, and the data of Figs. 24 and 25 are illustrative. As in the case of the nitric, sulphuric, and acetic

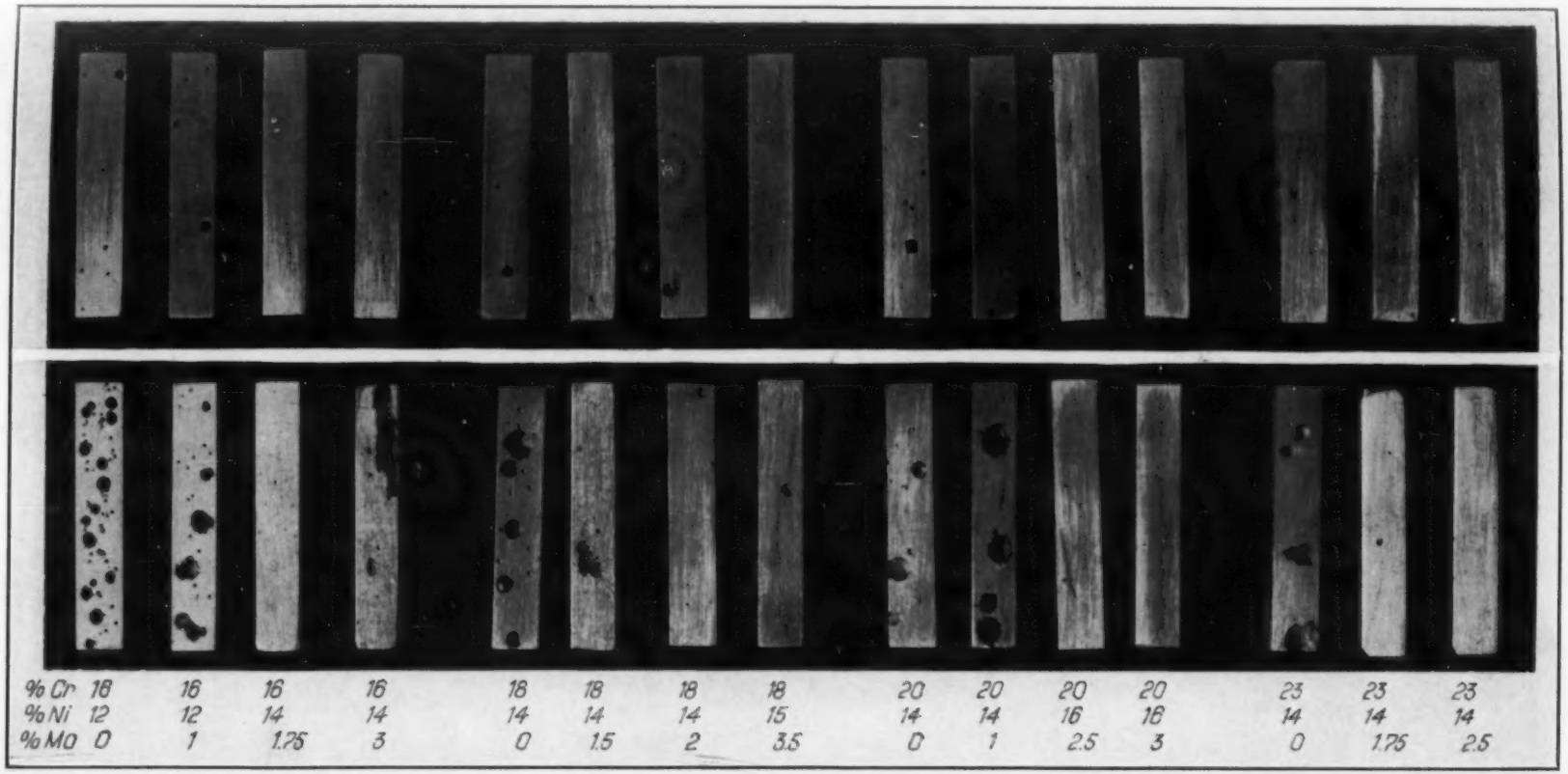

Fig. 24—Results of Pitting Tests on Molybdenum-Bearing Steels in Ferric Chloride Solutions Containing 10 Per Cent Sodium Chloride After 72 Hours' Immersion. Top Row—Tests Made in 0.5 Per Cent Ferric Chloride Solution Containing 10 Per Cent Sodium Chloride. Bottom Row—Tests Made in 5 Per Cent Ferric Chloride Solution Containing 10 Per Cent Sodium Chloride.

Fig. 25—Results of Pitting Tests on Molybdenum and Columbium-Bearing Steels in Ferric Chloride Solutions Containing 10 Per Cent Sodium Chloride After 72 Hours' Immersion. Top Row—Tests Made in 0.5 Per Cent Ferric Chloride Solution Containing 10 Per Cent Sodium Chloride. Bottom Row—Tests Made in 5 Per Cent Ferric Chloride Solution Containing 10 Per Cent Sodium Chloride.

acid tests, the data selected for presentation were obtained on practically austenitic steels; i.e., the steels contained enough nickel to make them austenitic after air cooling from 1100 to 1150 degrees Cent. (2010 to 2100 degrees Fahr.).

The data show that if the chromium content of the steels is below 18 per cent and in the neighborhood of 16 per cent, the addition of molybdenum improves resistance to pitting in these solutions, but the improvement is not so great as when the chromium content is 18 per cent or slightly higher. As the chromium content is raised further to 20 per cent and above, an additional improvement in resistance to pitting is obtained with a given molybdenum content. The data also show that when the chromium content is at least 18 per cent, the 2 per cent molybdenum steels are quite resistant to pitting and a further increase in molybdenum content to 3 per cent does not greatly change the results. When the chromium is somewhat in excess of 20 per cent, the molybdenum content can be reduced to approximately 1.50 per cent and lower, without sacrificing resistance to pitting under the conditions herein described.

Conclusions

This investigation has revealed that to avoid the development of the sigma phase, which is likely to cause difficulty, the low-carbon steels containing between 16 and 25 per cent chromium, 8 and 22 per cent nickel and from 1 to 4 per cent molybdenum should be balanced with respect to chromium, nickel and molybdenum contents. The proportion of sigma in the steels is governed largely by the chromium and molybdenum contents. By reducing the molybdenum content to 2 per cent or slightly lower, a low-carbon fully austenitic steel containing approximately 18 to 19 per cent chromium and 12 to 14 per cent nickel practically free of sigma formation is obtained. The sigma constituent in the higher molybdenum content steels may be partly responsible for the difficulties met with in hot working these steels, and the indications are that if the molybdenum content is reduced to about 2 per cent, the resulting product will be far more readily hot-worked. Unless the higher molybdenum content steels are in the annealed condition the precipitated carbides and the sigma that forms reduce corrosion resistance. Under certain corrosion conditions the higher molybdenum (3 to 3.5 per cent) content steels may be preferred but it should be emphasized that they must be employed in the annealed condition to avoid the ill effects of both

sigma formation and carbide precipitation. The sigma phase that develops on heating the higher molybdenum content steels at the stress-relieving temperatures causes a serious lowering in toughness.

As stated above, a practical solution to the problem is secured by controlling the molybdenum content. A good range of molybdenum content for the austenitic steels containing 18 to 19 per cent chromium, and 12 to 14 per cent nickel is between 1.50 and 2.25 per cent. These steels have good resistance to pitting, are as resistant to oxidizing media as the higher molybdenum steels, and are practically as resistant to the reducing type of media, such as sulphuric acid and acetic acid vapors and condensate as the higher molybdenum content steels.

The 2 per cent molybdenum steels, however, are also subject to intergranular corrosion and should contain columbium to obtain a metal free of this defect. In order to obtain optimum resistance to the ill effects of intergranular corrosion the columbium content should be at least ten times the carbon content, but in most instances a columbium content of at least six times the carbon content is sufficient. After stress-relieving at 870 degrees Cent. (1600 degrees Fahr.), the lower columbium to carbon ratio steels are practically immune to intergranular attack.

In the annealed condition the 2 per cent molybdenum steels containing both ratios of columbium to carbon have as satisfactory resistance to both oxidizing and reducing types of corrosion as the steels without columbium, and this high degree of corrosion resistance remains substantially unimpaired when the steels are heated at the stress-relieving temperatures of about 870 degrees Cent. (1600 degrees Fahr.). Thus the columbium addition to these 2 per cent molybdenum steels renders them far more practical for general use, but as emphasized above, the molybdenum content should be controlled because the columbium addition will eliminate only the ill effects of carbide precipitation, and will not prevent the sigma formation in the steels containing 3 per cent or more molybdenum.

Acknowledgment

The authors wish to express their appreciation for the co-operation received from the management and members of the staff of the Union Carbide and Carbon Research Laboratories, Inc. Their thanks are given especially to the management for their permission to publish these data.

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3. H. Hougardy, "The Brittle Constituent in Chromium-Nickel-Iron Alloys," *Metal Progress,* Jan. 1940, p. 64.

DISCUSSION

Written Discussion: By R. David Thomas, Jr., metallurgical engineer, Arcos Corp., Philadelphia.

We are indeed grateful to Mr. Franks and his associates for a fine piece of fundamental research on an alloy which is becoming increasingly important. To those of us who have experimented with additions of columbium to either a Type 316 or Type 317 alloy, the structural diagrams presented in this paper are especially significant.

Our work on these alloys has been in connection with obtaining a weld metal of properties comparable to those obtained in plate material—a problem which must go hand in hand with the development of any alloy which is to be joined by arc welding. In the course of our development we discovered that the addition of 0.50 per cent columbium to a Type 317 (3.0 to 3.5 per cent molybdenum) alloy gave a weld metal which was definitely hot-short. The ductility of the as-welded tensile sample was reduced from 47 per cent in 2 inches on the non-columbium-bearing weld metal to 6 per cent in the same weld metal with 0.50 per cent columbium. By reducing the nickel from 13.5 to 11 per cent in a columbium-bearing Type 317 weld metal, a weld deposit free from hot-short cracks was obtained.

The reduction of the nickel content will probably be objected to by the authors of this paper in view of their experimental work. We are reporting these tests to show how the development of weld metals may yield different results from those arrived at by experimenting with wrought alloys.

Perhaps the explanation of the hot-shortness in the high nickel deposit might be explained if we knew more about the equilibrium diagram with respect to temperature and composition. In welding, the rapid chilling yields dendritic segregations which may throw part of the alloy into the sigma phase region at a high temperature where its strength is extremely low, thus giving hot-short cracks. By reducing the nickel, the initial precipitation of more ferrite at the high temperature may decrease the degree of segregation and consequently the amount of the sigma phase constituent.

This discussion so far is somewhat academic since we recognize and have also proved by laboratory tests that the columbium stabilized Type 317 alloy is impracticable for service, even if a crack free weld metal is produced. However, the same applies to a lesser degree in the columbium stabilized Type 316 weld metal, namely, that too high a nickel content tends to give hot-short cracks. Consequently, for welding an alloy containing 2.0 to 2.25 per cent molybdenum

and 0.50 per cent columbium, we find it is safer to specify nickel 11.0 to 13.0 per cent rather than 12 to 14 per cent which Mr. Franks finds desirable for wrought alloys.

Written Discussion: By R. H. Thielemann, research laboratory, General Electric Co., Schenectady, N. Y.

This paper is certainly a valuable contribution to the understanding of the austenitic stainless alloys. The authors are to be complimented on the thoroughness and completeness of their investigation.

From these results it becomes increasingly clear that the metallurgy of the chromium-nickel austenitic alloys containing appreciable additions of molybdenum, silicon, columbium and tungsten is by no means simple.

Apparently, in these low carbon alloys, loss of toughness and of corrosion resistance can result from two distinct causes:

(1) Precipitation of carbides from solid solution to grain boundaries after prolonged heating.

(2) Formation of sigma constituent after prolonged heating.

With the occurrence of either phenomenon, toughness and corrosion resistance can be temporarily restored by rapid cooling, or annealing, from above the temperature of solid austenite solution. After this treatment, alloys in the first class, providing no ferrite is formed, will be nonmagnetic, and, according to the authors, those in the second class will be magnetic. This means that carbide precipitation is due to unstable austenite whereas the sigma formation is due to unstable ferrite. But since the formation of ferrite in the second case is also due to the instability of austenite, it is hard to see why the alloys will be magnetic if rapidly cooled from above the temperature of solid austenitic solution. Would the authors expect to find the retention of austenite possible if quenching instead of air cooling were employed?

The authors state that they were able to separate the sigma constituent from one of their alloys by an electrolytic method. The writer would like to ask if they were able to analyze this constituent for the elements present. To find this constituent rich in the ferrite-forming elements, such as chromium, molybdenum and silicon, would be expected.

As the authors have pointed out, it seems likely that additions of columbium to these alloys should promote the formation of the sigma constituent. In fact, additions of any of the ferrite-forming elements should act in this manner, and to overcome this effect increased additions of austenite-forming elements, such as nickel and manganese, would be necessary.

In view of these results, and from experience with these alloys, it seems to the writer than an adoption of modified composition limits for the KA2SMo or Type 316 alloy by the various producers should be in order. With the present composition range, it is evident that alloys will be susceptible to sigma formation after short exposures at elevated temperatures. Also, if these alloys are to be welded, the transformation of austenite to ferrite on cooling is not desirable. With the formation of the sigma constituent, as the authors point out, corrosion resistance and toughness are decreased. Also there are indications that both high temperature creep and rupture properties are decreased. The following composition range in per cent would seem desirable: Carbon 0.10

max., manganese 1.5-2.0, silicon 0.40-0.60, chromium 17-19, nickel 13-15, molybdenum 1.75-2.25.

Written Discussion: By M. A. Scheil, research metallurgist, A. O. Smith Corp., Milwaukee.

The authors are to be complimented on their splendid contribution to the metallurgy of stainless steels. This paper is timely in view of what has been known to date concerning "balanced" compositions. The authors have covered a wide range of composition in their research and have recorded the usual analysis determined for these alloys.

In view of the fact that nitrogen and oxygen are present in all chromium-nickel alloys it would seem to the writer rather pertinent to the problem to have included a nitrogen and oxygen analysis on several of the alloys. The amount of nitrogen and oxygen and its combination in the alloy is certainly a factor in the hot-shortness characteristics of these alloys as shown some time ago by Newell Hamilton.[1] The nitrogen content may also have a bearing upon the formation of sigma phase and the attendant brittleness of the higher molybdenum alloys. In this connection, it would be interesting to have the nitrogen analysis for the alloys given in Table III. It would also be of interest to learn from the authors whether the notch brittle condition they observed in the high molybdenum alloys of Table III after heating at 1400 and 1600 degrees Fahr. disappeared when these alloys were tested at temperatures above room temperature.

The authors in their conclusions refer to the reduced corrosion resistance of the higher molybdenum alloys as being partly due to the effect of sigma formed at 1600 degrees Fahr. The writer would be particularly interested to learn if any nitric acid corrosion tests were made on heats Nos. E-520 and E-504 shown in Table III after heating 72 and 350 hours at 1600 degrees Fahr. It would furthermore be of interest to compare these results with similarly tested samples that had been reheated 4 hours at 1200 degrees Fahr. It would appear to the writer that this should aid in an answer to the question of the corrosion loss resulting from formation of sigma.

The data of Fig. 17 and Table V bear out the authors' conclusions regarding the lowering of corrosion resistance to oxidizing media when the alloys are heated at 1600 degrees Fahr. for 4 hours. Had the authors increased the time of heating from 4 hours the results would have shown a closer approach to the annealed heat treated condition. However, for the purposes of comparison with the columbium stabilized chromium-nickel-molybdenum alloys, the authors have probably chosen a heating time which was sufficient to retain their corrosion resistance after heating at the stress relieving temperature of 1600 degrees Fahr.

One criticism I have of the data that are reported in this paper is that the average corrosion penetration rates are given and this, of course, may be very misleading, especially if the penetration rate figure is increasing rapidly on each period of exposure.

It is hoped that the authors will continue their work on these alloys in the future.

[1]American Institute of Mining and Metallurgical Engineers, Iron and Steel Division, 1934.

Written Discussion: By Stephen F. Urban, Carnegie-Illinois Steel Corp., Chicago.

The authors are to be complimented on completing so detailed a research to demonstrate that austenitic stainless steels containing molybdenum do not behave in the manner commonly anticipated. They have shown clearly that when desirable or beneficial results are obtainable by the addition of a given increment of an element, it cannot be assumed without further study that additional increments will result in further improvement in the property in question.

Even more important, the authors have shown that large increases in the molybdenum content of stainless steels yield a set of properties inferior to similar compositions of lower molybdenum content. The writer and his associates have had similar experiences and offer the following remarks by way of confirmation and, in certain instances, additional data.

Our work had its inception with the observation that quenched stainless steels containing sufficient molybdenum to yield some ferrite in the structure, thereby making the steels somewhat magnetic, become nonmagnetic after reheating to about 1400 to 1800 degrees Fahr. Like the authors, we have identified the decomposition product of ferrite as the sigma constituent which was first observed by Bain and Griffiths in the straight chromium and higher chromium-nickel alloys. Likewise, in the course of our microscopic study we found it very difficult to preserve the sigma constituent since it was rapidly attacked by many etching reagents, thus indicating that corrosion properties might be adversely affected by its presence. That this is true has been ably demonstrated by the authors, in that corrosion resistance of molybdenum-bearing steels in sulphuric acid and acetic acid condensate is not improved by molybdenum content in excess of approximately 2 per cent (for the usual 18-8 analysis). Further, the hot-working properties of the higher molybdenum steels are considerably impaired. Thus we find that some of our standard analyses are inferior in corrosion resistance to lower molybdenum steels and that we have brought upon ourselves unnecessary fabricating problems. In connection with the latter, the writer and his associates have repeatedly found that the higher molybdenum alloys are difficult to hot work and become excessively so if the usual amounts of columbium or titanium are added in conjunction with a high molybdenum content.

The data pertaining to corrosion resistance in nitric acid are even more interesting than those for sulphuric acid or acetic acid condensate, in that the resistance in nitric acid may, for some treatments, be worse at 3 per cent molybdenum than with 2 per cent.

Again referring to the sulphuric acid corrosion data, the writer wishes to emphasize that quenched, and quenched and stress relieved, steels without columbium are as satisfactory as columbium-bearing steels. This is clearly shown by the data in the paper (Figs. 20 and 21).

In regard to the effect of the sigma constituent on the pitting type of corrosion, there do not appear to be sufficient data to justify a positive statement. The indications, however, are that the sigma constituent adversely affects pitting resistance. As a partial confirmation, the writer and his associates have found two heats of steel, of the following composition, which were superior in pitting resistance to other heats tested:

Heat	C	Mn	Si	Cr	Ni	Mo
A	0.07	1.39	0.40	18.51	10.85	1.98
B	0.06	1.71	0.45	18.96	13.56	3.08

Heat A was tested for three years in sea water and was much superior to all other samples on the same rack. Heat B was tested by accelerated laboratory tests. Both of the compositions shown were characterized by unusually good pitting resistance even though there is a considerable difference in composition between the two. In Heat A there was no sigma because of the low molybdenum content, whereas Heat B, notwithstanding the high molybdenum content, is free of sigma because of its high nickel content.

From the data given by the authors it is evident that the amount of sigma formed is related to the balance between the amount of austenite and ferrite-forming elements contained in the alloy; i.e., ratio of the nickel to the chromium, molybdenum, columbium or titanium content. In addition to this we found that, contrary to expectations, apparently manganese did not act as an austenite former, but rather as a ferrite former. Thus, increasing the manganese content promotes the formation of sigma (perhaps by accelerating its range of formation) as illustrated by the following data:

Analyses							Sigma After 3 Hours at		
							1600	1700	1800
C	Mn	Si	Cr	Ni	Mo	Cb	Degrees Fahr.	Degrees Fahr.	Degrees Fahr.
0.05	0.57	0.49	17.50	10.34	3.11	0.55	1%	2%	4%
0.05	0.92	0.51	17.69	10.40	3.06	0.62	2%	4%	4%
0.05	1.91	0.50	18.00	10.17	3.00	0.53	5%	5%	5%
0.07	2.80	0.41	17.87	10.42	3.06	0.60	5%	5%	15%

In all cases S less than 0.01 per cent and P less than 0.025 per cent.

It appears that the last sentence on page 44 of the article may be misinterpreted to mean a number of things. First, the statement applies to alloys that have been heated in the range of temperature in which carbide precipitation occurs. Secondly, it implies that the molybdenum present would be more effective for corrosion resistance in a columbium-bearing steel, heated in the range referred to, by virtue of the fact that none of the molybdenum would be associated with carbon. This does not appear to be true for alloys of 8 to 10 per cent nickel and molybdenum in excess of 2 per cent because a greater effective molybdenum content would produce more sigma, thereby probably reducing the corrosion resistance.

With reference to the impact data shown in Figs. 13 to 16 inclusive, the authors conclude that the loss in impact strength at 1400 and 1598 degrees Fahr., for steels containing over 2 per cent molybdenum, is due to the formation of large amounts of sigma. The steels selected for impact testing, however, were of such composition that they should be free of sigma, using Figs. 1 to 12 inclusive as a basis for reference. From this it appears that the positions of the lines separating the various fields in Figs. 1 to 12 inclusive would be considerably altered by the longer periods at temperature. This appears to be indicated by the findings of Schafmeister and Ergang (Archiv für das Eisenhüttenwesen, Vol. 12, pages 459-465, 1939). In any event, the authors show that long period stress-relieving cycles reduce the impact strength when the molybdenum content is greater than 2 per cent. The loss in impact strength for

high molybdenum contents is even greater in the presence of such stabilizing elements as columbium. On the other hand, stabilizing elements are not needed to overcome intergranular corrosion, provided that long-time stress-relieving cycles are employed. The following data show conditions under which intergranular corrosion may be avoided:

Composition in Per Cent				
Carbon 0.07	Manganese 0.72	Silicon 0.45	Chromium 17.85	Nickel 10.00

Treatment	Increase in Resistance in Per Cent	Remarks
Quenched from 1975 degrees Fahr., 16 hours at 1550 degrees Fahr., slow cooled at 25 degrees Fahr. per hour to 1100 degrees Fahr.	+130	—
Same as above plus 100 hours at 1200 degrees Fahr.	Very large	Samples completely disintegrated
Forged, 16 hours at 1550 degrees Fahr., slow cooled at 25 degrees Fahr. per hour to 1100 degrees Fahr.	+0.45	—
Same as above plus 100 hours at 1200 degrees Fahr.	+1.30	—
Forged, 72 hours at 1550 degrees Fahr., slow cooled at 25 degrees Fahr. per hour to 1100 degrees Fahr.	−0.20	—
Same as above except 100 hours at 1200 degrees Fahr.	+1.10	—

The above data pertain to samples treated as shown and subsequently exposed for 72 hours to boiling copper sulphate solution. It is true that in the above tests, the quenched material was susceptible to intergranular corrosion in spite of the subsequent "stress-relieving" treatment, but the material in the as-forged condition was not susceptible even after 100 hours at a sensitization temperature.

While the steel referred to contains no molybdenum, ample data are available (see Table VI also) to show that the presence of this element does not greatly reduce susceptibility to intergranular corrosion. Presumably the above data may logically be used to interpret the behavior of molybdenum-bearing steels under similar conditions.

Oral Discussion

P. A. E. ARMSTRONG:[3] I thank our chairman for the honor of being asked by him to extemporaneously discuss this excellent paper.

Unfortunately, I did not see a copy of this paper until about one hour before the meeting, therefore cannot discuss the subject matter in close detail. I have, however, conducted a number of investigations on alloys of this type and analysis given in this excellent paper. Therefore, I feel that I may be able to contribute something to the subject.

It is well known that sigma phase can be produced in high-chromium steels free from nickel or substantial amounts of manganese. It is also known that sigma phase can be produced in similar steels when nickel or manganese is present in substantial quantities. Manganese is an excellent accelerator of the formation of the sigma phase.

The so-called high-melting-point elements, such as W, Mo, Ta, Ti, Zr, Cb, and Si, are sigma-phase-forming elements in varying degrees. Furthermore, when they are used, particularly together, they generally increase the sigma phase. Nickel will also act the same way, particularly when silicon is about 2

[3]Metallurgist, Westport, Conn.

per cent or more. When manganese is used with low silicon and with nitrogen, the hard phase is produced. For instance, a steel alloy of about 24 to 25 per cent chromium plus 5 per cent manganese and about 0.30 per cent nitrogen will, when reheated to 1400 to 1600 degrees Fahr., show the characteristic hardness and loss of toughness that is common to the sigma phase. If the manganese is replaced with nickel, and especially in the presence of about 2 per cent silicon, similar hardness results are obtained. Columbium will, when used in an alloy of about 20 to 25 per cent or more chromium, with nickel about 5 to 14 per cent, produce the sigma phase, on reheating to about 1500 degrees Fahr., providing columbium is carried to a few per cent. Should silicon also be employed in a similar alloy, the sigma phase is readily produced.

It is an interesting fact that such an alloy containing insufficient amounts of silicon to produce a marked sigma-phase characteristic, or where a similar alloy is used and the columbium is insufficient to produce a marked sigma-phase manifestation and the same quantities of silicon and columbium used together, there will be produced a marked sigma-phase precipitation. Therefore, the two together are mutually accelerating in the formation of the sigma phase. A similar thing is true, as so ably shown in the authors' paper. Columbium, when present, increases the amount of sigma phase that can be developed in an alloy containing molybdenum.

Mr. Benno Strauss had issued to him a patent on June 8, 1926, No. 1,587,614, for a chromium-nickel steel containing molybdenum, his range chromium 18 to 30 per cent, nickel 4 to 20 per cent, molybdenum 2 to 4 per cent, and carbon up to about 0.40 per cent. This form of stainless steel was recommended for resistance to sulphurous acid attacks at high temperatures and pressures. The alloy had excellent strength.

I showed much earlier than this that molybdenum could be used with the stainless type of chromium-nickel alloys, and especially those containing silicon, and I also was aware that magnetic alloys of this type could be made nonmagnetic and hard by heat treatments at temperatures around about 1400 degrees Fahr., and somewhat lower or higher. I ran into this condition when adapting this class of material for carburizing box and annealing tube uses which embraced these temperatures, and I found that a tough material could readily be turned into one that was hard and brittle.

Mr. Peter Payson published a paper, Technical Publication No. 464, Annual Meeting, A.I.M.E., February, 1932. He submitted a large number of alloys including chromium and molybdenum alloys, containing low carbon and 20 per cent or more of chromium, 8 per cent or more of nickel, and molybdenum under and over 3 per cent, and when he submitted these alloys to heat for 15 hours below and above 1400 degrees Fahr., he found that these alloys, which were decidedly magnetic when cooled down from forging or annealed, became practically nonmagnetic. Therefore, he was aware of the formation of the so-called sigma phase and its accompanying hardness and brittleness.

Dr. John A. Matthews, early in 1934, wrote that KA-2 steel, standard specification, 18-22 chromium, nickel 6.5 to 10 per cent, molybdenum 2 to 4 per cent, when heated for prolonged periods between 1000 to 1400 degrees Fahr. caused the alloy when cooled to undergo a phase change accompanied by loss

of magnetism, increased hardness, and lowering of impact resistance. Obviously, this is proof of the formation of the sigma phase. I would refer you to "The Book of Stainless Steels," second edition, published by the American Society for Metals.

The rolling of 18-8-type alloys with molybdenum gives trouble. The edges will crack, and the surface will show signs of cracking or tearing. This is not, in my opinion, due to the formation of the sigma phase, as the temperature is too high for it to form and the time factor too short as the heat falls. The trouble, in my opinion, is due to mixed crystals of ferrite and austenite, which have very different plasticity, when at rolling temperatures. Therefore, this class of alloy should be so proportioned as to chromium and nickel with molybdenum as to be wholly austenitic, and the diagrams of Figs. 1 to 12 of the authors' paper clearly show the amount of chromium and nickel with the required molybdenum that must be employed to produce a wholly austenitic alloy, and the specifications for chromium-nickel steels with molybdenum used are very often clearly of the mixed-crystal variety.

I hope that the authors' very excellent paper will have the effect of adjusting the nickel and chromium content of these alloys in conjunction with the molybdenum employed so that they are wholly austenitic, either in the annealed condition or when drawn to about 1600 degrees Fahr. for prolonged periods. The present type alloys, when made into pressure vessels which must of necessity be welded, might have in the vicinity of the weld a sigma-phase area, and any stress relieving around about 1600 degrees Fahr. would tend to produce the sigma phase and all of its possible troubles.

When the sigma phase is formed, and if we consider sigma phase to be a precipitated FeCr compound, then it might be the loss of corrosion resistance to be a form of chromium depletion in highly dispersed areas, similar to the theory accompanying the precipitation of chromium carbide. This would account for the loss of corrosion resistance, as the authors have so ably demonstrated. Maybe now that the authors have isolated some crystals within the sigma-phase area, they may be able to prove or disprove this assumption.

I have selected a few alloys from a few thousand that I have personally melted and tested, which included the investigation of various alloys of this general class, and the hardness that can be obtained in them by reheating to about 1400 degrees Fahr., and they all show that the sigma-phase type of hardness can be produced over quite a range of compositions.

A nickel-free high-chromium steel alloy, containing molybdenum, is subject to the sigma-phase type of hardness.

All of the alloys tested were given substantially the same heat treatment, namely, they were heated to 2100 degrees Fahr., for about 10 minutes and water quenched. They were then tested for Rockwell C hardness and as to whether they were magnetic or nonmagnetic. All of the following alloys which were quenched from this temperature were tough, and when reheated to 1450 degrees Fahr. for 15 hours and air-cooled, the Rockwell C hardness is given and also information as to whether they were magnetic or nonmagnetic. When given this heat treatment, the hardness was substantially increased, many became nonmagnetic even though they were all magnetic to start with. The hardness pro-

duced was accompanied with loss of ductility. Some were brittle and others were strong, but would only take a slight bend before breaking. The following analyses clearly bring out these points:

Per Cent
C — 0.45
Cr —28.0 } Heated to 2200 degrees Fahr., W.Q.—RC 27—Magnetic—Tough
Mn — 0.75

Ni — 0
Si — 0.75 } Reheated to 1400 degrees Fahr. 15 hours, A.C.—RC 46—Magnetic—Very Brittle.
Mo — 3.5

Per Cent
C — 0.10
Cr —25.0 } Heated to 2100 degrees Fahr., W.B.—RC 26—Magnetic—Tough.
Mn — 0.50

Ni — 7.0
Si — 2.0 } Reheated to 1400 degrees Fahr. 15 hours, A.C.—RC 37—Magnetic—Strong—Low Impact.
Mo — 1.0

Per Cent
C — 0.10
Cr —25.0 } Heated to 2100 degrees Fahr., W.Q.—RC 26—Magnetic—Tough.
Mn — 0.5

Ni — 7.0
Si — 2.0 } Reheated to 1400 degrees Fahr. 15 hours, A.C.—RC 41—Very Slightly Magnetic—Strong—Low Impact.
Mo — 2.0

Per Cent
C — 0.10
Cr —25.0 } Heated to 2100 degrees Fahr., W.Q.—RC 26—Magnetic—Tough.
Mn — 0.5

Ni — 7.0
Si — 2.0 } Reheated to 1400 degrees Fahr. 15 hours, A.C.—RC 47—Nonmagnetic—Strong—Low Impact.
Mo — 3.0

Per Cent
C — 0.10
Cr —26.0 } Heated to 2100 degrees Fahr., W.Q.—RC 27—Magnetic—Tough.
Mn — 2.5

Ni — 7.5
Si — 0.5 } Reheated to 1400 degrees Fahr. 15 hours, A.C.—RC 34—Magnetic—Strong—Tough.
Cb — 3.0

Per Cent
C — 0.10
Cr —26.0 } Heated to 2100 degrees Fahr., W.Q.—RC 27—Magnetic—Tough.
Mn — 2.5

Ni — 7.5
Si — 2.0 } Reheated 1400 degrees Fahr. 15 hours, A.C.—RC 45—Nonmagnetic—Strong—Tough.
Cb — 2.0

Per Cent
C — 0.40
Cr —26.0 } Heated to 2100 degrees Fahr., W.Q.—RC 27—Magnetic—Tough.
Mn — 2.5

Ni —10.0
Si — 3.0 } Reheated to 1400 degrees Fahr. 15 hours, A.C.—RC 43—Nonmagnetic—Strong—Tough.
Cb — 2.0

Per Cent
C — 0.40
Cr —28.0 } Heated to 2100 degrees Fahr., W.Q.—RC 27—Magnetic—Tough.
Mn — 2.5

Ni — 8.0
Si — 0.5 } Reheated to 1400 degrees Fahr. 15 hours, A.C.—RC 63—Non-
Cb — 6.0 magnetic—Brittle.

Per Cent
C — 0.40
Cr —28.0 } Heated to 2100 degrees Fahr., W.Q.—RC 25—Magnetic—Tough.
Mn — 2.5

Ni —15.0
Si — 0.5 } Reheated to 1400 degrees Fahr. 15 hours, A.C.—RC 47—Non-
Cb — 6.0 magnetic—Strong—Tough.

Per Cent
C — 0.40
Cr —28.0 } Heated to 2100 degrees Fahr., W.Q.—RC 30—Magnetic—Tough.
Mn — 2.5

Ni — 8.0
Si — 3.0 } Reheated to 1400 degrees Fahr. 15 hours, A.C.—RC 63—Non-
Cb — 3.0 magnetic—Fairly Strong—Low Impact.

Per Cent
C — 0.40
Cr —25.0 } Heated to 2100 degrees Fahr., W.Q.—RC 29—Magnetic.
Mn — 0.50

Ni — 7.0
Si — 2.0 } Reheated 1400 degrees Fahr. 15 hours, A.C.—RC 47—Nonmag-
Ta — 1.65 netic—Strong—Low Impact.
Cb — 1.35

Per Cent
C — 0.40 } Heated to 2000 degrees Fahr., W.Q.—RC 24—Magnetic.
Cr —25.0

Mn — 9.50 } Reheated 1400 degrees Fahr. 15 hours—RC 40—Nonmagnetic—
Si — 0.80 Brittle.

Per Cent
C — 0.40 } Heated to 2000 degrees Fahr., W.Q.—RC 30.
Cr —25.0

Mn — 9.0 } Reheated 1400 degrees Fahr. 15 hours, A.C.—RC 46—Nonmag-
Si — 2.0 netic—Brittle.

Per Cent
C — 0.45
Cr —25.0 } Heated to 2200 degrees Fahr., W.Q.—RC 26—Magnetic.
Mn — 0.50

Ni — 5.0
Si — 2.5 } Reheated 1400 degrees Fahr. 15 hours, A.C.—RC 43—Magnetic—
Ti — 0.86 Strong—Fairly Tough.
N — 0.30

Although the sigma phase does produce brittleness, it also produces hardness and stiffness in both the hot and cold condition. Therefore, providing that some toughness is retained in the cold, and the corrosion resistance is sufficient for the job, these heat treated sigma-phase-type alloys will find a useful place. For instance, valves and turbine blades call for strength and stiff-

ness at elevated temperatures, and the alloys that I am talking about would find a use in this application and doubtless many others. Therefore, the sigma-phase manifestations should not condemn this class of alloy for a number of uses.

The authors did not give hardness figures or physical properties. These would be extremely useful in conjunction with the Izod values given in their paper. Incidentally, Rockwell C hardness values are not consistent if the alloy is not sigma phase over its entire surface, and hard and soft spots exist. For this reason, Brinell hardness is not readily translated into Rockwell C figures as the large area tested measures groundmass of variable characteristics.

I think it is clear from the authors' excellent work that putting more of an element that produced increased corrosion resistance may get one into trouble, or give unlooked-for results. In other words, one or two pills may be good, but the whole box might ruin an otherwise good product.

R. H. THIELEMANN:[3] There is one more question which I should like to ask Mr. Franks. As I understand it, after the alloys with high molybdenum content were cooled from the solid solution temperature they were found to be magnetic and on reheating to 870 degrees Cent. they became nonmagnetic. On this reheating did you make dilatometer curves to see if there is change in volume occurring with the formation of the sigma constituent? I think such information would throw some light on how the formation of the sigma constituent takes place. It seems quite possible that the sigma constituent may be the insoluble nonmagnetic compound remaining from the partial solution of the ferrite phase in austenite at this temperature.

Authors' Reply

The authors greatly appreciate the widespread interest shown by the discussion of this paper, and it is clear from the discussion that the attempts being made to enhance the properties of the molybdenum-bearing 18-8 steels will receive serious consideration.

Mr. Thomas states that for welding a steel containing 18 per cent chromium, 2 to 2.25 per cent molybdenum, and 0.5 per cent columbium it would be safer to specify a nickel content from 11 to 13 per cent to avoid the development of cracks due to hot-shortness of the welded metal. The question of how much nickel should be present in the welding rod is difficult to answer at present because of lack of service tests. However, we do not believe that the nickel content should fall below 12 per cent, especially if the weld requires stress-relief. In this case, it is important that the nickel content be high enough to prevent the formation of appreciable quantities of sigma in the weld deposit.

Mr. Scheil raises a number of points. Although all the steels shown in Table III were not analyzed for nitrogen, it can be safely stated that they contain between 0.03 and 0.06 per cent of this element. The impact tests were made at room temperature after the samples were exposed to the elevated temperatures indicated. These data, therefore, refer to room temperature

[3]Research laboratory, General Electric Co., Schenectady, N. Y.

toughness. The following table shows the results of corrosion tests in a boiling 65 per cent nitric acid solution on samples of a commercial type 317 stainless steel.

	Per Cent
Chromium	17.92
Nickel	13.61
Manganese	1.87
Silicon	0.37
Molybdenum	3.30
Carbon	0.07

Condition of Metal	Corrosion Rate—In. Pen. Per Month—First 48-Hr. Period	Second 48-Hr. Period	Third 48-Hr. Period
Annealed	0.00093	0.00088	0.00095
Annealed: reheated 4 hr. at 650 degrees Cent. and A.C.	0.0059	0.127	.....
Annealed: reheated 4 hr. at 870 degrees Cent. and A.C.	0.0013	0.0025	0.0047
Annealed and heated 4 hr. at 870 degrees Cent. and A.C. Reheated 4 hr. at 650 degrees Cent. and A.C.	0.0011	0.0014	0.0028
Annealed: reheated 72 hr. at 870 degrees Cent. and A.C.	0.0013	0.0016	0.0023
Annealed and heated 72 hr. at 870 degrees Cent. and A.C. Reheated 4 hr. at 650 degrees Cent. and A.C.	0.0016	0.0032	0.0084

A.C. = air-cooled.

It is evident from these data that particle size plays an important role. If the sigma phase is coagulated by heating at 870 degrees Cent. its effect on corrosion resistance is not so great as when it is finely divided; for example, when it is formed at 650 degrees Cent.

The corrosion data were given as an average rate for the sake of brevity. We agree with Mr. Scheil that often this may be misleading. However, the data as presented show the general trend, as the increase in the corrosion rate with each period was far greater for the chromium-nickel steels containing only molybdenum than for the steels containing both molybdenum and columbium.

In referring to the sulphuric acid data, Mr. Urban states that the annealed and stress-relieved steels without columbium are as satisfactory as the steels containing columbium. Figs. 20 and 21 may be misleading on this point, and we refer him to the data of Tables X and XI, which show lower corrosion rates for the steels containing columbium after stress relieving. He has indicated that manganese increases the rate of formation of sigma in the 18-8 steel containing molybdenum. His conclusion is based upon a short heating period. The probability is that all the steels described by him would show the same amount of sigma, regardless of the manganese content if heated for a somewhat longer period.

The possibility of avoiding intergranular corrosion failures by special heat treatment has often been considered. As Mr. Urban has shown, certain heat treatments when applied to the 18-8 steel in the as-forged condition can be used to eliminate this type of corrosion. This means of prevention, however, is not satisfactory when it is necessary to weld the steel during fabrication. Also the need for a stabilizing element in the steel becomes necessary in order to retain full corrosion resistance. The decrease in resistance to general corrosion might easily offset the improvement in regard to intergranular attack.

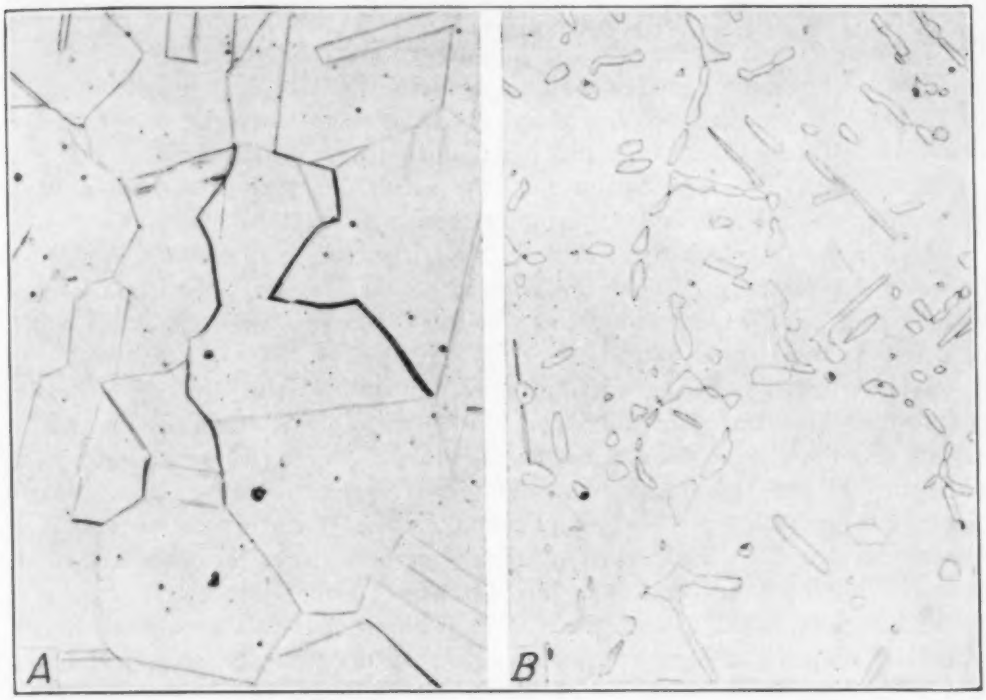

Fig. A—Photomicrograph Showing Structure of Steel Containing 18.22 Per Cent Chromium, 13.64 Per Cent Nickel, 1.75 Per Cent Manganese, 0.59 Per Cent Silicon, 3.67 Per Cent Molybdenum and 0.05 Per Cent Carbon Heated 5 Minutes at 1100 to 1150 Degrees Cent. and Air-Cooled. The Structure is Austenitic. × 500.

Fig. B—Photomicrograph of Steel Shown in Fig. A After Heating About 600 Hours at 870 Degrees Cent. and Air Cooling. The Metal in this Condition Was Quite Brittle. Its Structure Consists of Austenite and Sigma Particles. × 500.

In connection with Mr. Thielemann's discussion it should be stated that only those steels that are deficient in nickel are magnetic when rapidly cooled from the annealing temperature. On the other hand, Figs. A and B of this reply to discussion show definitely that sigma can be formed from a fully austenitic molybdenum-bearing chromium-nickel steel.

The results of chemical analysis made on a sample of the residue obtained from the metal shown in Fig. B are given in the table below.

Composition of Residue Separated by Electrolyte Method from Heat E500 After Air Cooling from 1100 to 1125 Degrees Cent. and Holding 672 Hours at 870 Degrees Cent. and Air Cooling

Original Composition of Steel—Per Cent		Composition of Residue
Chromium	18.22	23.38
Nickel	13.64	5.03
Molybdenum	3.67	12.54
Manganese	1.79	1.44
Silicon	0.59	2.10
Carbon	0.05	0.57
Iron	Remainder	44.40

These data indicate that a large part of the molybdenum, carbon, silicon, and chromium are segregated in the sigma constituent.

Mr. Thielemann in his preferred analysis has set the nickel content for the 2 per cent molybdenum steel containing no columbium, between 13 and 15 per cent. The authors prefer that the nickel content be kept in the range 11 to 13 per cent on account of economics. Dilatometer tests were not used to determine volume changes in the metal during the formation of sigma, but we agree with Mr. Thielemann that the results of such tests would be of great interest. At the first opportunity these tests will be made.

It is indeed a pleasure to receive Mr. Armstrong's discussion in view of his wide experience in the development of stainless steels. He has submitted considerable data which add greatly to the value of the paper, and which need not be commented upon.

Mr. Armstrong points out that in instances involving the use of valves and turbine blades at elevated temperatures, alloy steels containing controlled amounts of the sigma phase are quite applicable. We agree with him on this statement, because the purpose of the present paper is not to condemn the sigma-bearing steels for such applications. The object is to provide soft, ductile and tough molybdenum-bearing low-carbon austenitic chromium-nickel steels having optimum resistance to corrosion under the greatest variety of conditions. As stated in the paper, it is believed that this result can be obtained by reducing the molybdenum content to about 2 per cent, and otherwise arranging the composition to obtain the fully austenitic steels with and without columbium.

TRANSFORMATION OF AUSTENITE ON CONTINUOUS COOLING AND ITS RELATION TO TRANSFORMATION AT CONSTANT TEMPERATURE

By R. A. Grange and J. M. Kiefer

Abstract

The transformation of austenite in S.A.E. 4340 steel as it occurs on cooling at constant rate was studied experimentally by the metallographic method. The resulting data were employed in the construction of an experimental cooling transformation diagram analogous to the isothermal diagram. The structure and hardness resulting from cooling this steel to room temperature at any constant rate are shown by charts.

The general relationship of transformation on continuous cooling and transformation at constant temperature is discussed and a simple empirical method for estimating cooling transformation phenomena from isothermal data proposed. When applied to the S.A.E. 4340 steel, the derived cooling diagram is in excellent agreement, from a practical standpoint, with the cooling diagram determined experimentally. When the isothermal diagram is known, this empirical method thus enables us to tell what happens as the result of any known rate of cooling of austenite, and to derive a possible fundamental index of hardenability.

Introduction

AUSTENITE cooled continuously below the minimum temperature at which it can exist indefinitely as a stable phase does not begin immediately to transform. When cooling is extremely slow, the transformation proceeds substantially at the equilibrium temperature; faster cooling progressively lowers the temperature at which transformation begins and it then proceeds over a *range* of temperature. For a given austenite, the cooling rate determines the temperature range over which the transformation actually takes place and hence the character and mechanical properties of the final structure.

In order to separate the influence of temperature and of time

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upon the resultant structure, Davenport and Bain (1)[1] studied austenite transformation at a series of constant temperature levels. Since this pioneering work, they and others have continued the investigation of constant temperature, or isothermal transformation, and at the present time isothermal transformation diagrams (S-curves) are available for most common grades of steel (1), (2), (3), (4). These diagrams show precisely the effect of temperature level

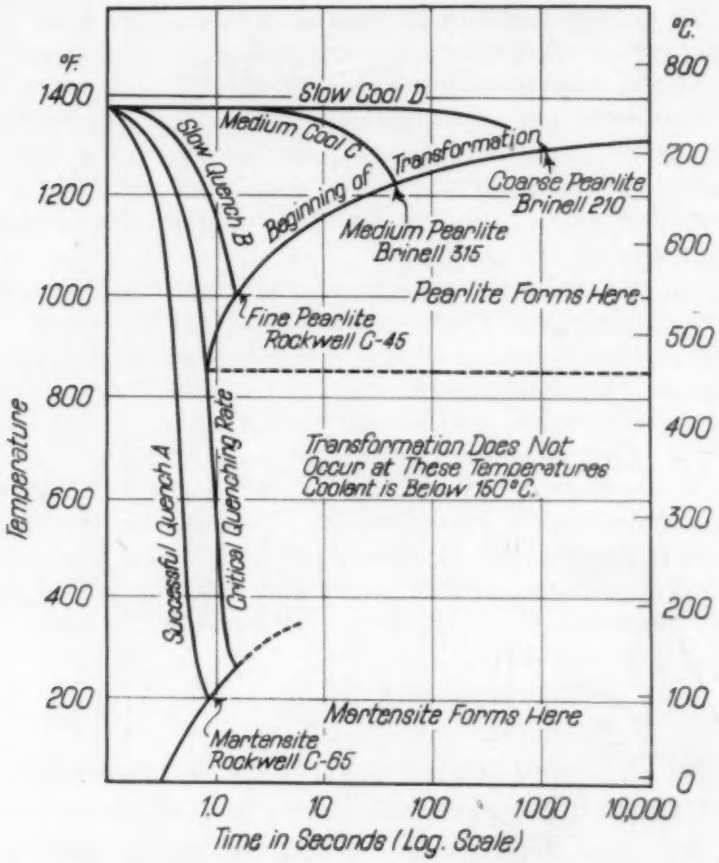

Fig. 1—Schematic Representation of the Relation Between Cooling Rate and Temperature of Initial Transformation on Cooling (Bain).

upon the time required for the measurable beginning and ending of transformation and upon the character and hardness of the isothermal product. The fundamental character of the isothermal diagram and its importance in understanding the heat treatment of steel is fully recognized; this diagram can, however, be quantitatively applied only when austenite is made to transform at substantially constant temperature.

[1]The numbers in parentheses pertain to the list of references appended to the paper.

Davenport (2) has pointed out the need for correlating the transformation phenomena during continuous cooling with isothermal data and has outlined the principles of a "cooling transformation diagram". Bain (5), in 1932, published the schematic cooling diagram for 0.85 per cent carbon steel, reproduced in Fig. 1, which shows the curve for the beginning of transformation and the structures produced by several typical cooling rates. The Ar′ range is clearly associated with transformation to pearlite at and above the fastest reacting region "nose" of the isothermal diagram (S-curve); the middle, or bainite, region, which is "sheltered" by the nose, is missing. This diagram relates cooling curves only to the visible beginning of transformation, but it is obviously possible to go a step further and to include on a similar diagram a curve representing the completion of transformation for various cooling rates; on such a diagram the Ar′ region would be a zone within which the austenite transforms to pearlite. The diagram would depict for transformation on continuous cooling what the S-curve does for the isothermal case, and would be quantitatively adaptable to any heat treatment involving a known cooling rate. This type of diagram, which is the subject of the present paper, may be constructed from appropriate experimental observations, and it can also be derived from the isothermal diagram by a simple method; as will be shown, both procedures yield results which, for practical purposes, are identical.

The most informative method of studying isothermal transformation is the metallographic examination of specimens that have been held at constant temperature for appropriate periods. Details have been described elsewhere (1), (2); the basic principle is shown in a chart published by Davenport (2) and reproduced in Fig 2A. For isothermal study, specimens are cooled very rapidly from the austenitizing (heating) temperature, held for a predetermined period (P_1, P_2, P_3, etc.) in a constant temperature bath, then withdrawn and immediately quenched in water or brine to room temperature; for the cooling study, Fig. 2B, similar specimens are cooled continuously at a predetermined rate from the austenitizing temperature to a predetermined temperature (T_1, T_2, T_3, etc.), then, just as before, withdrawn and immediately quenched to room temperature. In either case any untransformed austenite remaining in the specimen at the instant it was quenched to room temperature appears in the final structure as martensite, which is readily distinguishable from the transformation product formed at the higher temperature prior to

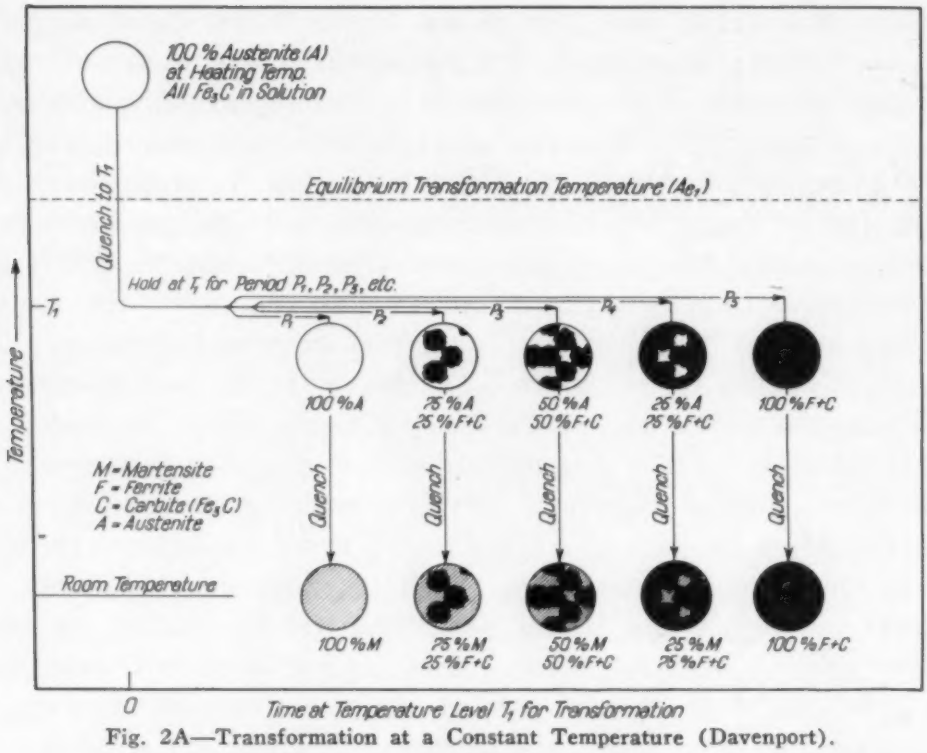

Fig. 2A—Transformation at a Constant Temperature (Davenport).

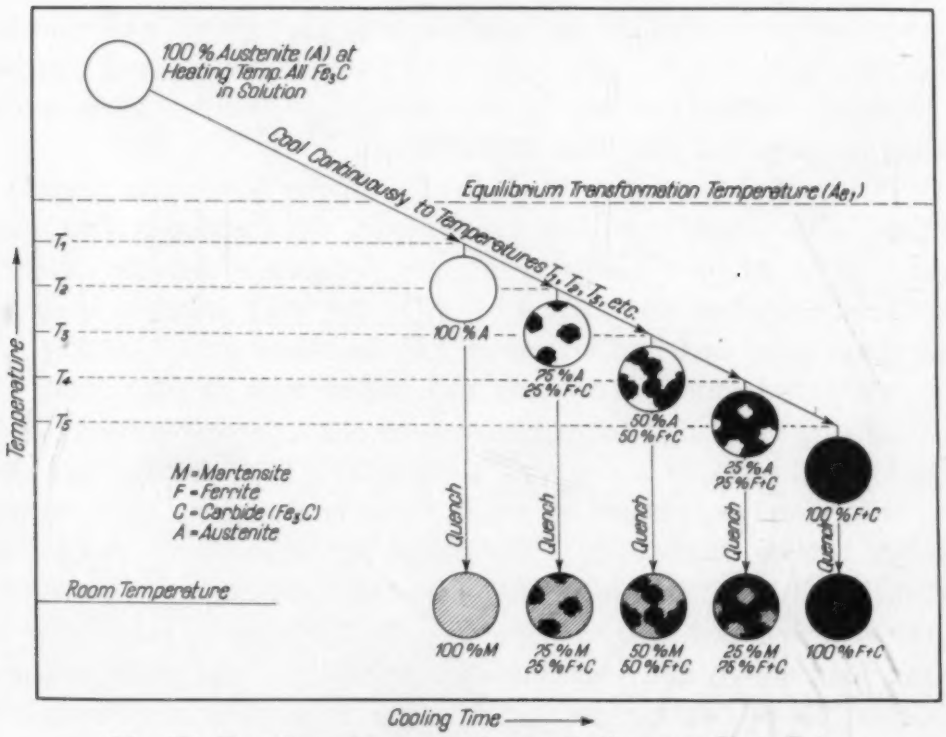

Fig. 2B—Transformation on Continuous Cooling at a Given Rate.

Figs. 2A and 2B—Schematic Representation of the Heat Treating Operations Involved in the Metallographic Method of Measuring the Progress of Austenite Transformation.

the final quench. The diagrams of Fig. 2 are schematic and do not necessarily represent what would be observed in practice; in general, the exploration of a given temperature level (isothermal technique) or a given cooling rate (cooling technique) requires more specimens than the charts show. It is to be noted that in the isothermal case the structure formed at any single temperature level is uniform, whereas, on continuous cooling, transformation proceeds over a *range* of temperatures and the final structure is therefore a mixture or a series of products, each product being substantially indistinguishable from what forms isothermally at the same temperature. Just as the development of an isothermal diagram requires exploration of many temperature levels, the experimental determination of a cooling diagram requires the investigation of several different cooling rates. The cooling diagram consists of lines drawn through points indicating the measurable beginning and ending of transformation located on each respective cooling curve at the proper temperature and time; a logarithmic, or ratio, scale of time is necessary in order to include a suitable range of cooling rates and at the same time to show detail in that portion of the diagram referring to relatively fast cooling. It thus summarizes on a single chart the results of observations of austenite transformation along a series of cooling curves just as the isothermal diagram does for a series of constant temperature levels.

The direct experimental investigation of transformation on cooling is extremely difficult except in steels whose alloy content renders the austenite very slow to transform; in comparison, the isothermal diagram may be determined for most common grades of steel with relative ease. Moreover, precise experimental determination of a cooling diagram by the metallographic method requires that the observer be able to recognize the character of the aggregates comprising the structure; this is difficult, particularly for alloy steels, unless the isothermal structures have been previously studied. Thus it is far more convenient to derive a cooling diagram from isothermal data, if a satisfactory method of derivation can be developed, than to determine it experimentally, especially as a considerable number of isothermal diagrams are now available for this purpose. Isothermal diagrams may, however, be inaccurate, particularly with regard to the beginning line at the "nose" in fast-reacting steels, and to both the beginning and ending lines in the region just below the equilibrium transformation temperature (Ae_1); in the derivation of a cooling diagram these inaccuracies are necessarily included and pos-

sibly magnified. On the other hand, it is to be noted that for the rapidly transforming steels in the temperature range in which the time is very short, some uncertainty in the precise time required is of no practical significance. It is mainly the fact that the isothermal diagram has been, or can readily be, determined for most common steels, whereas the precise experimental determination of a cooling diagram is limited to a few sluggish alloy steels, which makes it desirable to have a simple method for deriving the cooling diagram from isothermal data.

Experimental Cooling Diagram for S.A.E. 4340 Steel

The experimental determination of the cooling diagram is facilitated if the steel chosen is one whose isothermal diagram indicates

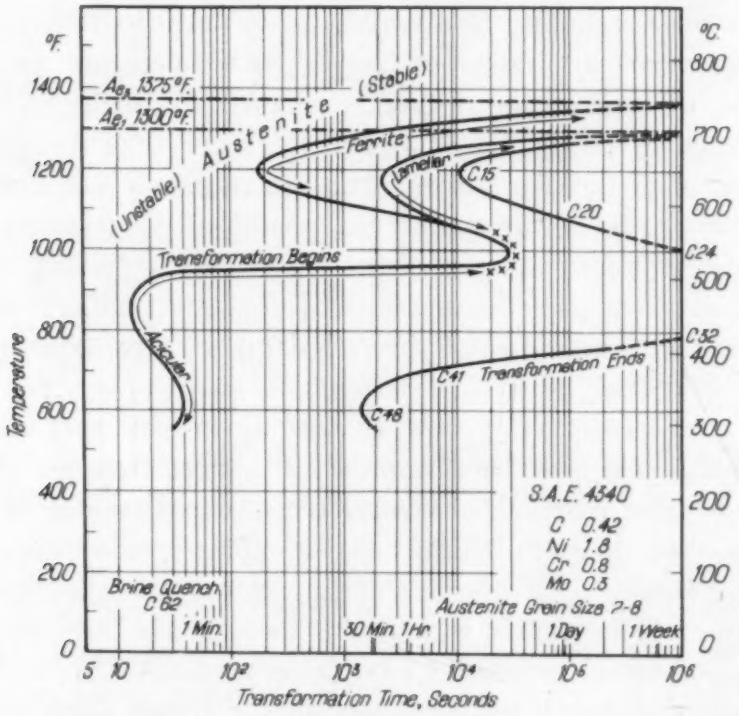

Fig. 3—Isothermal Transformation Diagram for S.A.E. 4340 Steel (Davenport).

very sluggish transformation behavior. For this reason, the steel selected as an example was the S.A.E. 4340 grade; its isothermal diagram has been published (2) and is reproduced in simplified form in Fig. 3. As originally presented, it included a field in the neighborhood of 900 degrees Fahr. (480 degrees Cent.) in which a structure tentatively designated as "X" was found to form; in Fig. 3 this

field has been omitted and the structure "X" will, for simplicity, be regarded herein as a high temperature form of bainite. Since the microstructures formed isothermally below about 550 degrees Fahr. (290 degrees Cent.) in this steel are almost indistinguishable from the martensite formed on quenching, the diagram has not been carried below 550 degrees Fahr. (290 degrees Cent.); any structure formed below this temperature will be regarded as martensitic in character, even though its hardness may be somewhat lower than that of fully hard martensite in steel of this composition.

The specimens used were taken from the identical bar, and given the same austenitizing treatment, as those used for determining the isothermal diagram of this steel. Pertinent data are listed in Table I.

Table I
Data on the S.A.E. 4340 Steel Investigated

	C	Mn	Si	Ni	Cr	Mo
Composition	0.42	0.78	0.24	1.79	0.80	0.33

Preliminary Treatment—Hot-rolled 1¼ inches round, normalized from 1800 degrees Fahr.
Specimen Size—1¼ inches diameter, half disks $\frac{1}{8}$ inch thick
Austenitizing Treatment—1550 degrees Fahr. for 15 minutes
Austenite Grain Size No. 7-8 A.S.T.M.

Equilibrium Transformation Temperatures	Ae_1	Ae_3
	1300 degrees Fahr.	1375 degrees Fahr.

The progress of austenite transformation during cooling was followed by metallographic examination of a total of 104 specimens, representing seven different constant cooling rates. Every effort was made to cool at constant rate, and this was accomplished by means of a rate controlling device attached to the furnace; the rate controller was not adaptable to the fastest rate attempted and, in this case, cooling unavoidably occurred at a slightly diminishing rate. Owing to the slow rate of transformation of this steel, the evolution of heat during transformation (recalescence) did not prevent the attainment of a constant rate of cooling. The experimental technique consisted, briefly, of heating a number of specimens at 1550 degrees Fahr. (845 degrees Cent.) for 15 minutes, and then cooling in the furnace; at each of a series of successively lower, predetermined temperatures during the cooling, one specimen was withdrawn and quenched to room temperature. Metallographic examination of such specimens made it possible to follow the progress of transformation during continuous cooling at each controlled rate. Typical microstructures produced at various stages in the transformation as the austenite was cooled at a rate of 10 degrees Fahr. per hour are shown in Fig. 4;

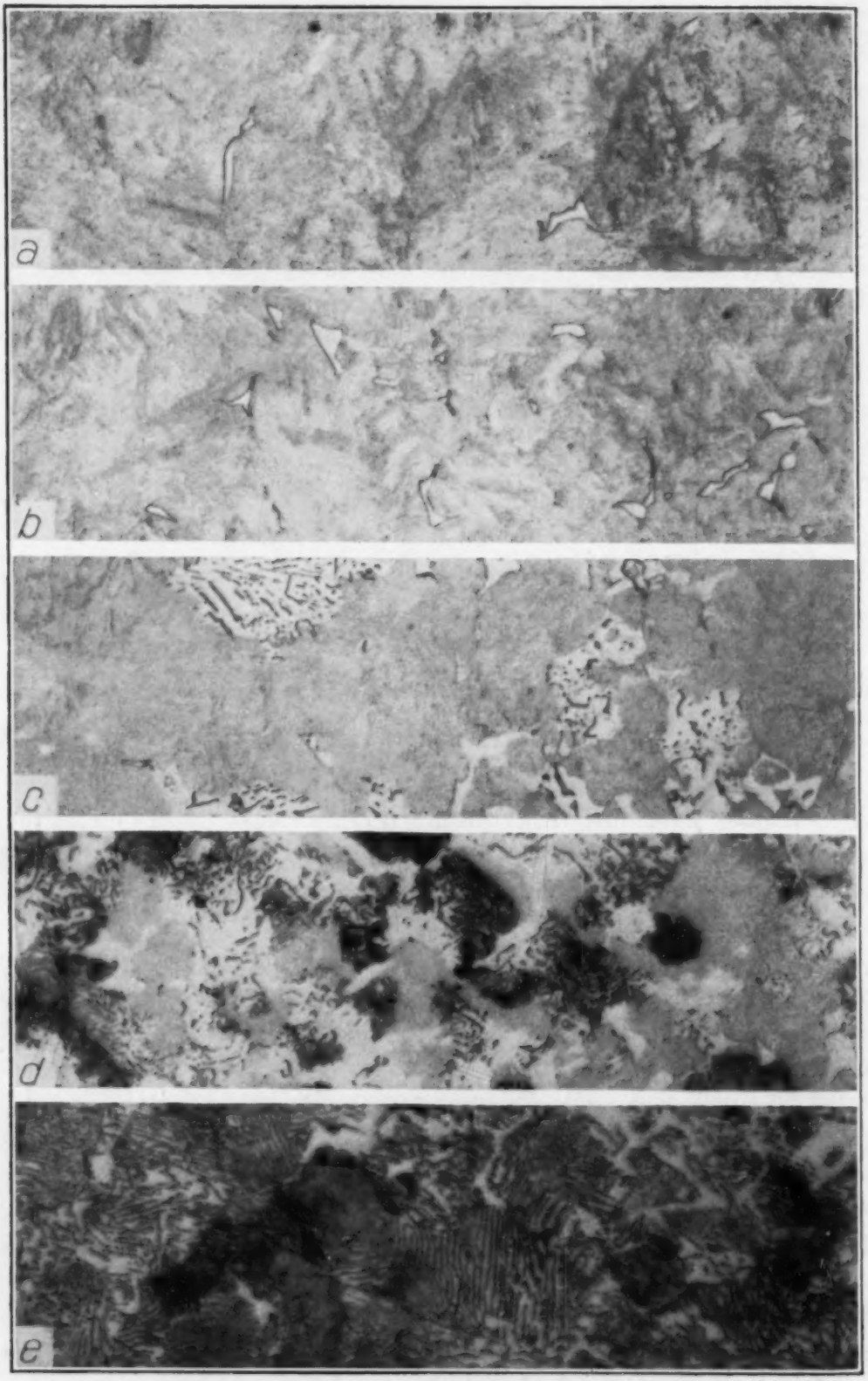

Fig. 4—Progress of Austenite Transformation in S.A.E. 4340 Steel Cooled from 1550 Degrees Fahr. at 10 Degrees Fahr. Per Hour. Magnification × 1000.
(a) Cooled to 1285° F.; (b) to 1265° F.; (c) to 1235° F.; (d) to 1200° F.; (e) to 1180° F.

at this cooling rate the austenite began to transform at about 1330 degrees Fahr. (720 degrees Cent.) and transformation was complete at 1180 degrees Fahr. (640 degrees Cent.). The first stage in the reaction is the rejection of proeutectoid ferrite and this is followed by transformation to lamellar pearlite. The first pearlite forms at 1235 degrees Fahr. (670 degrees Cent.) and is relatively coarse; as cooling proceeds, the new pearlite forming is finer and finer. The series of structures illustrated in Fig. 4 is less complex than a series taken during a faster cooling; at 100 degrees Fahr. per hour, for example, the transformation temperature range is much greater and the structure consists, in the later stages, of mixtures of ferrite and both lamellar and acicular ferrite-carbide aggregates. From such observations it is clear that the character of the structure formed at any instant during the cooling is indistinguishable from that produced by isothermal transformation at the same temperature.

The initial step in the construction of the experimental diagram consists of plotting temperature-time curves for the several cooling rates employed. Actually, cooling in all cases commenced at the austenitizing temperature (1550 degrees Fahr.), but since the significant cooling began only after the austenite reached its equilibrium transformation temperature, a more fundamental type of diagram results if the cooling curves are plotted as beginning at the Ae_3 temperature for the transformation to proeutectoid ferrite, and at the Ae_1 temperature for transformation to pearlite or bainite. In this way the cooling diagram gives the time interval necessary to decompose austenite after it has become unstable, and is therefore on the same basis with respect to time as the isothermal diagram. In Fig. 5 each cooling rate is accordingly represented by two curves, one plotted as beginning at the Ae_3 temperature (curves A′, B′, C′, etc.) and the other, as beginning at the Ae_1 temperature (curves A, B, C, etc.). From microscopic observation of the structure, the temperatures at which ferrite, pearlite or bainite was observed to begin to form or to stop forming were plotted on the proper cooling curve (A′, B′, C′, etc., for ferrite, A, B, C, etc., for pearlite or bainite). These temperatures are designated in Fig. 5 by shaded zones instead of by points because the experimental observations were not sufficiently numerous to determine them with greater precision. Curves drawn through these zones and properly labelled comprise the experimental cooling diagram shown in Fig. 5. The final structure resulting in each case from continued cooling to room temperature is

indicated near the bottom of the chart. This diagram is not quite complete in that transformation during cooling at a constant rate faster than Curve A was not studied; the range of rates studied does, however, suffice to give the practically significant portion of the

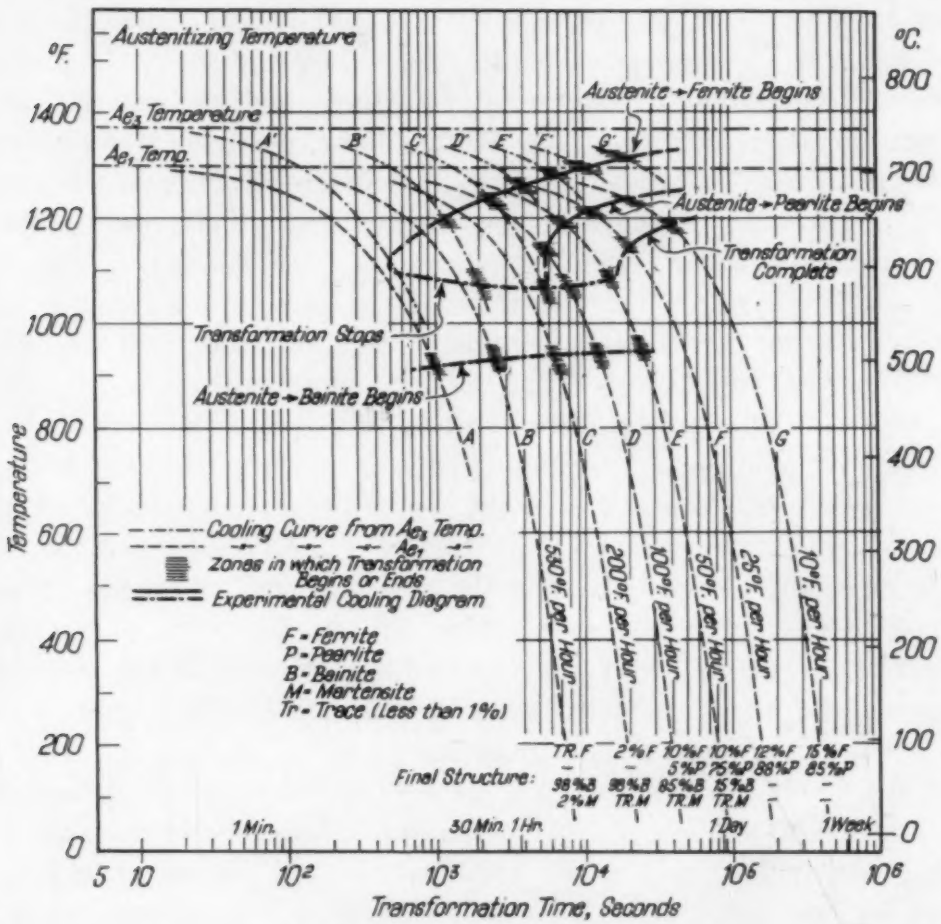

Fig. 5—Diagram Showing Austenite Transformation in S.A.E. 4340 Steel on Continuous Cooling at Constant Rate. Based Upon Experimental Observations.

diagram. No curves representing the end of transformation to bainite, or the beginning or ending of transformation to martensite, are shown for the reason that no suitable criterion is available for distinguishing metallographically between low temperature bainite and high temperature martensite. Structures forming below about 550 degrees Fahr. (290 degrees Cent.) in this steel have the appearance of martensite and in the final structure are so designated.

Cooling Diagram for S.A.E. 4340 Steel Derived from the Isothermal Diagram

Experimental study of cooling transformation in several grades of low alloy steel, including the S.A.E. 4340 just described, resulted in the development of an empirical method for deriving a cooling diagram from the isothermal diagram. The essence of this method consists of representing any stage of the cooling by a point on the isothermal diagram which indicates, by its position, the equivalent amount of transformation that has occurred on cooling to that temperature at the specified rate; the details of the steps involved will be discussed later.

For the construction of the derived diagram a series of curves, each representing a constant rate of cooling, are plotted to scale on the isothermal diagram, cooling above the equilibrium transformation temperature being again neglected; for each cooling rate two curves, one commencing at the Ae_3 temperature, the other at the Ae_1 temperature, are plotted. The amount of transformation at successive stages for each cooling rate is then estimated by the empirical method to be described in detail later; the significant temperatures at which transformation either begins or ends are joined by the curves that comprise the final cooling transformation diagram. Reasonably accurate construction of such a diagram necessitates the use of a large sheet of semilog paper.

A diagram so constructed is shown in Fig. 6; in order to avoid a confusing number of lines on the chart, many details of its construction have been omitted. Of the many cooling curves plotted, only the four significant ones associated with the appearance or disappearance in the final structure of a type of structural constituent (martensite, ferrite, bainite or pearlite) are shown. The derived cooling diagram is represented by heavy lines, labelled to indicate their significance; the corresponding isothermal diagram from which the cooling diagram was derived is shown in light lines. Fig. 6 is a complete cooling diagram showing the measurable start and finish of transformation in terms of temperature and cooling time below the equilibrium transformation temperature, also the character of the final structure for any constant rate of cooling. For types of cooling other than at constant rate the diagram would not necessarily be quite the same, and this fact must be borne in mind in the quantitative application of the diagram to actual heat treating. According to the

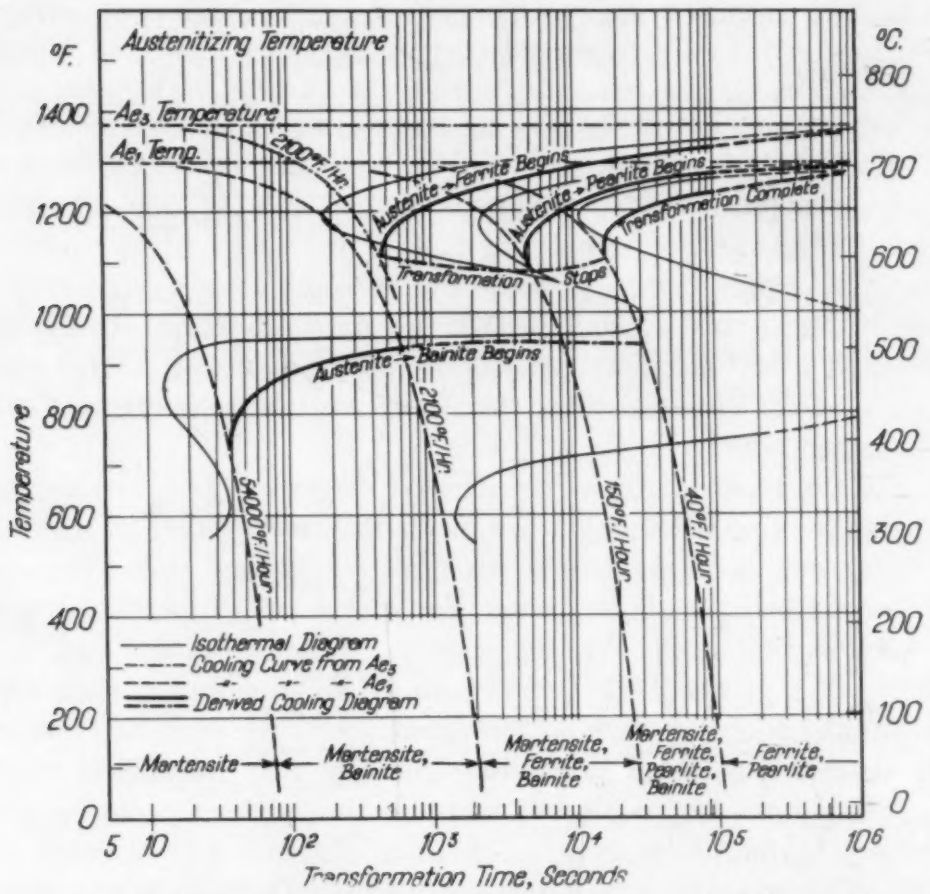

Fig. 6—Diagram Showing Austenite Transformation on Cooling at Constant Rate in S.A.E. 4340 Steel. Derived from Isothermal Data.

derived diagram, cooling S.A.E. 4340 steel at a rate ranging from 54,000 degrees Fahr. per hour to 40 degrees Fahr. per hour produces a decreasing amount of martensite in the final structure; at constant rates less than 40 degrees Fahr. per hour the austenite transforms completely in the Ar′ region to a relatively soft structure consisting of ferrite and pearlite.

Experimental and Derived Cooling Diagrams Compared

Comparison of the experimental diagram (Fig. 5) with the derived diagram (Fig. 6) reveals that they are, on the whole, very similar; indeed, in practice, deductions drawn from either would be identical. The location of the curves comprising the experimental cooling diagram was (in a number of instances) not determined with exactness; hence some judgment, based on experience, was used in

drawing these curves and a somewhat closer agreement between derived and experimental diagrams is entirely possible on the basis of actual data. The only important discrepancy lies in the location of the curve representing the completion of the pearlite reaction; the experimental curve is somewhat lower than the derived curve although the location of the former was confirmed by examination of a number of specimens. It is thought that the discrepancy may be due to lack of isothermal data between 1200 degrees Fahr. (650 degrees Cent.) and the Ae_1 temperature; since the beginning and ending lines for isothermal transformation in this region were not precisely located, the cooling transformation lines derived from them will of course be uncertain to the same extent. Another explanation for this discrepancy may be that during the very slow cooling necessary to complete the transformation to pearlite, the long sojourn at temperatures just below 1550 degrees Fahr. (845 degrees Cent.) resulted in some coarsening of the austenite grains which would, of course, tend to increase the time required for completion of transformation.

Relation of the Cooling Diagram to the Isothermal Diagram

The cooling diagram for S.A.E. 4340 steel (Fig. 5 or 6) differs appreciably from its isothermal diagram (Fig. 3). Curves comprising the cooling diagram lie below and to the right of the corresponding isothermal curves. The portion of the isothermal diagram between 950 and 1050 degrees Fahr. (510 and 565 degrees Cent.) is "sheltered" by the pearlite "nose" and so is missing in the cooling diagram. In other words, the slow forming structures produced by long isothermal treatment in this temperature range do not form at all during continuous uniform cooling. It is, however, probable that a very small and practically immeasurable amount of transformation can occur during cooling at certain rates through the 1050 to 950 degrees Fahr. (565 to 510 degrees Cent.) temperature range, but from a practical standpoint the reaction can simply be regarded as temporarily stopping while this steel cools through this range.

Unlike the plain carbon steel whose cooling diagram is illustrated in Fig. 1, the bainite-forming region in the diagram for the S.A.E. 4340 steel is not "sheltered" by the overhanging nose of the isothermal curve; accordingly bainite may be readily formed when S.A.E. 4340 steel is continuously cooled; in fact, as the diagram indicates,

rapid-etching acicular constituents occur in the final structure of S.A.E. 4340 steel within a considerable range of cooling rates. It is of interest to note that this steel has not only a cooling range in which pearlite and martensite form, but also an important intermediate cooling range in which rapid-etching acicular structures form. This type of transformation behavior has been found to be typical of many low alloy steels in which it appears that certain alloying elements of the carbide-forming type retard the transformation in the upper range of temperature where soft lamellar structures form, without a corresponding retardation in the intermediate region where rapid-etching acicular structures result from the transformation. Thus, steels of suitable composition may be transformed to the bainite type of structure by continuous cooling; this greatly increases the range of properties obtainable by continuous cooling and suggests interesting possibilities for heat treating such steels. Griffiths, Pfeil and Allen (3) and Wever and co-workers (6) have studied intermediate transformation in low alloy steels and their work is in agreement with these conclusions.

The lines of both the cooling diagram and the isothermal diagram are asymptotic to the equilibrium transformation temperature (Ae_1 or Ae_3) and both diagrams are practically identical in the region just below this temperature, provided that they refer to the same austenite grain size. In general the displacement (downward, or to the right) from their isothermal location, of the pair of curves representing the beginning and ending of transformation increases with faster rate of cooling up to the rate which just produces a fully martensitic structure. For a particular austenite, the significant minimum time interval for the beginning of transformation on the cooling diagram, at its "nose", is about three times as great as the corresponding minimum interval (the so-called nose) on the isothermal diagram, the temperature in the former case being of course lower than the latter. For instance, for our sample of S.A.E. 4340 steel, Fig. 6 shows the significant minimum time for beginning of isothermal transformation, at about 1200 degrees Fahr. (650 degrees Cent.), to be 180 seconds, whereas the corresponding minimum time on cooling, at about 1100 degrees Fahr. (595 degrees Cent.), is about 540 seconds, or three times as long.

In any comparison of the two types of diagrams, it is important to bear in mind the logarithmic scale of time on which they are plotted, for interpretations based on mere horizontal linear distances

on these charts may lead to erroneous conclusions unless repeated reference is made to the actual time intervals indicated on the logarithmic scale.

Relation Between Constant Cooling Rate, Structure, and Hardness at Room Temperature

In the course of the experimental work, hardness readings were taken on all specimens; in a general way they served as a check on

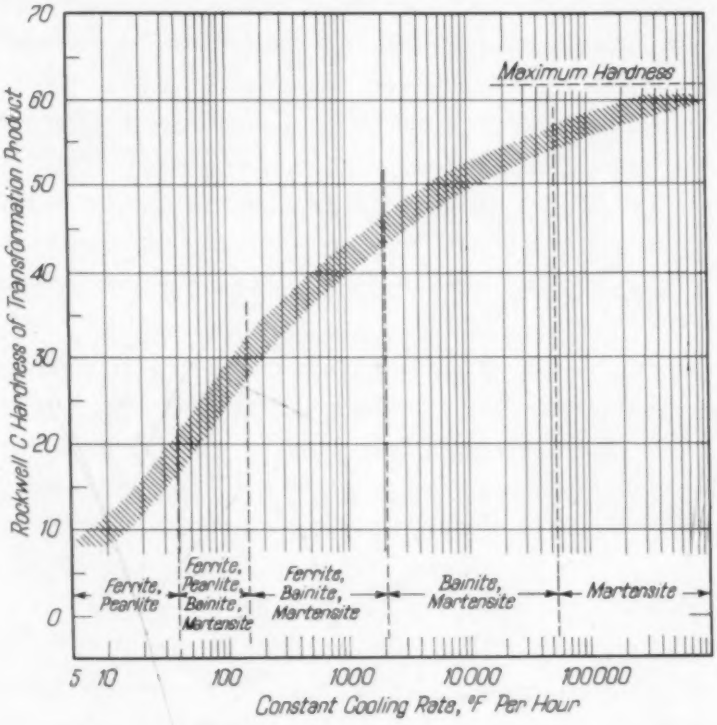

Fig. 7—Approximate Relation Between RC Hardness, Final Structure and Constant Cooling Rate for S.A.E. 4340 Steel.

the validity of the microscopic observations. These hardness data, supplemented by additional hardness measurements on specimens quenched in brine, water, oil and air, are plotted in Fig. 7 to show the relation between constant cooling rate and the final hardness and structure of S.A.E. 4340 steel cooled from 1550 degrees Fahr. (845 degrees Cent.) to room temperature. This relation is presented as a shaded band rather than as a single line because the experimental data did not warrant a more precise relationship. As the speed of cooling decreases from very fast (brine quench) to very slow, the hardness decreases from 62 RC to about 7RC, the corresponding differences in final structure being as indicated in Fig. 7.

Estimation from the Isothermal Diagram of the Progress of Transformation During Cooling at Any Constant Rate

In order to facilitate description of the method used for deriving from the isothermal diagram the corresponding diagram for any constant rate of cooling, a portion of the isothermal S-curve for a plain carbon eutectoid steel in the temperature range 900 to 1250 degrees Fahr. (480 to 675 degrees Cent.) is shown on an extended time scale in Fig. 8. The broken line, starting at the Ae_1 temperature, repre-

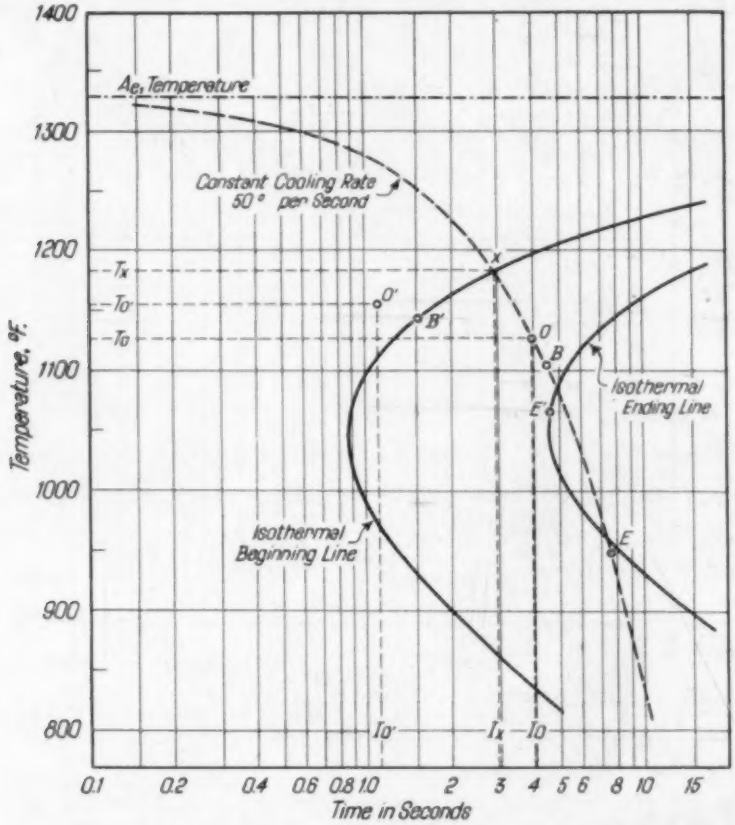

Fig. 8—Chart Showing a Portion of the Isothermal Transformation Diagram for Plain Carbon Eutectoid Steel and a Constant Cooling Rate of 50 Degrees Fahr. per Second Plotted from Ae_1 Temperature; Illustrates the Steps Involved in the Method for Relating Transformation on Cooling to the Isothermal Diagram.

sents a constant cooling rate of 50 degrees Fahr. per second from that temperature downward. It intersects the isothermal beginning line at the point X at a temperature T_X after a time interval I_X; let us take an arbitrary lower temperature T_O reached after the interval I_O, and consider what happens during cooling between points X and O.

If complex and tedious calculations are to be avoided, it is necessary to make two reasonable assumptions which, as will be shown later, are justifiable from a practical standpoint. These assumptions are:

1. That the extent of transformation of the austenite at the instant it cools to the intersection point X is not substantially greater than it would have been if quenched instantly to T_X; in other words, that some additional cooling time will be required before any measurable transformation occurs, in all cases of practical interest.

2. That on cooling through a limited temperature range, for example, T_X to T_O, the amount of transformation is substantially equal to the amount indicated by the isothermal diagram at the mean temperature $\frac{1}{2}$ $(T_X + T_O)$ after a time interval $I_O - I_X$.

When the austenite has cooled to point X, it would be necessary, on the basis of the first assumption, to hold it at the temperature T_X for an additional time interval nearly equal to I_X in order to form a visible amount of the transformation product. Under the conditions represented in Fig. 8, the austenite was not held at T_X but continued to cool uniformly. The additional interval after point X necessary to produce visible transformation will obviously be less than I_X since the isothermal beginning line shows that an ever shorter time interval is required for the beginning of transformation at lower and lower temperatures between T_X and T_O. The point at which visible transformation just begins on cooling can be graphically estimated on the basis of the principle of the second assumption; on this basis, the amount of transformation resulting from continuous cooling to point O is equal to that at the corresponding point O′ on the isothermal diagram, the co-ordinates of O′ being $T_{O'} = \frac{1}{2}$ $(T_X + T_O)$ and $I_{O'} = I_O - I_X$. Since the point O′ lies to the left of the isothermal beginning line, there has not yet been any visible amount of transformation; to determine where this will occur, it is necessary to select additional arbitrary later points on the cooling curve until, by trial and error, a point B is found for which the corresponding point B′, relocated as above, lies exactly on the isothermal beginning line. B is, then, the point of beginning of visible transformation when the steel is cooled at the rate of 50 degrees Fahr. per second.

As cooling proceeds beyond B, more and more transformation occurs, the progress of which can be estimated by selecting successively later points and ascertaining for each point the equivalent amount of isothermal transformation shown by the corresponding

relocated point on the isothermal diagram; this point is placed on the chart at the mean temperature after an interval equal to that spent in cooling from X to the point under consideration. In addition to the nominal 0 per cent and 100 per cent lines usually shown on the isothermal diagram, lines representing intermediate amounts of transformation may be plotted from adequate isothermal data; if this is done, the corresponding intermediate amount of transformation on cooling can be estimated more precisely. A point E will ultimately be reached whose equivalent isothermal transformation, represented by point E′, lies exactly on the isothermal ending line; at point E, therefore, cooling transformation will just have been completed.

For the conditions represented in Fig. 8, transformation on cooling at a rate of 50 degrees Fahr. per second began at 1105 degrees Fahr. (point B) and proceeded over a range of temperature down to 950 degrees Fahr. (point E), where it was just completed.[2] Observations of the structure produced by continuous cooling indicate that at any instant during the cooling it corresponds to that which would form isothermally at the same temperature. Therefore, although a relocated point such as E′ serves to show the relative amount of transformation on cooling, the character of the transformation product is that of a mixture of the isothermal structures that would be produced at temperatures between B and E.

An alternative method for estimating the visible beginning and ending of transformation on cooling, based upon the same assumptions as that just described and differing only in the details of the steps involved in the graphical analysis, is possible. In this case, the cooling curve of the steel is plotted on the isothermal diagram exactly as in Fig. 8. A point on the beginning line of the isothermal diagram at some temperature below X, for example, point B′, is first selected and a point B, representing the beginning of transformation on cooling, is located the same vertical distance below B′ on the chart as B′ is below X at a time $I_B = I_X + I_{B'}$. Point B′ is the only point on the isothermal beginning line which, when relocated in this way, lies exactly on the 50 degree Fahr. per second cooling curve; it must be found by arbitrarily selecting various points on the beginning line

[2]The methods for estimating the beginning of transformation on cooling from the isothermal diagram proposed by Steinberg (7) and by Hoyt (8), when applied to the present example, give a slightly higher value for the temperature at which transformation begins; no means for estimating the progress and the completion of transformation on cooling has been published by either of these authors.

of the isothermal diagram and, by trial and error, finding the corresponding point which lies on the actual cooling curve of the steel. E, the point representing the end of cooling transformation, is determined by relocating, in an analogous way, a point E′ which lies on the isothermal ending line. This procedure is, in effect, the reverse of the previous one, for here isothermal beginning (or ending) points are selected and relocated until the one is found that lies on any desired cooling curve and hence lies on the line representing the beginning (or ending) of transformation on cooling at this rate.

It is also possible, on the basis of the above assumptions, to determine the cooling rate at which transformation will visibly begin at any selected temperature. Let us assume that it is desired to determine for the steel whose isothermal diagram is shown in Fig. 8 the constant rate that will cause transformation on cooling to begin at the temperature T_B.[3] A series of constant rate cooling curves should, in this case, have been plotted on the isothermal diagram, but the steps involved may be explained without them. An arbitrary cooling rate, for example, the 50 degree Fahr. per second curve shown on Fig. 8, is chosen; it intersects the isothermal beginning line at point X and the temperature horizontal T_B at point B. A point B′ on the isothermal diagram, which represents an isothermal treatment equivalent to cooling at 50 degrees Fahr. per second to point B, is located at the temperature $T_{B'} = \frac{1}{2}(T_X + T_B)$ and at the time $I_{B'} = I_B - I_X$. Point B′ lies exactly on the isothermal beginning line, and hence 50 degrees Fahr. per second is the rate at which transformation on cooling begins at T_B. For any other rate of cooling, a relocated point analogous to B′ would not be on the isothermal beginning line. In practice, it would therefore be necessary to select successive arbitrary cooling rates until by trial and error the one is found for which a point analogous to B′ lies on the isothermal beginning line. In an analogous way, the cooling rate that will cause transformation to be just completed at any desired temperature can be determined. This procedure makes it possible to determine directly from the isothermal diagram the rate of cooling necessary to produce a given final structure.

The example illustrated in Fig. 8, which applies specifically to a plain carbon eutectoid steel in the Ar′ region of the isothermal dia-

[3] A specific temperature or time mentioned in this paragraph which does not appear in Fig. 8 refers to a point indicated by the "subscript"; for example, T_B refers to the temperature of point B, I_B refers to the time of point B, etc.

gram, was chosen because it is the simplest case. It is believed that this method of deriving cooling transformation data from the isothermal diagram is applicable to any part of the latter and to any plain carbon or low alloy steel, for the principles upon which it is based have been found to apply to all of the several grades of steel studied and to all types of structure with the exception of martensite. Before the method can be applied to any given case, the actual cooling curve of the steel must be plotted as beginning at the equilibrium transformation temperature, regardless of the temperature at which cooling actually began; that is, before plotting on the isothermal diagram, the time interval for cooling down to the equilibrium temperature (Ae_1 for pearlite or bainite) is subtracted from the total cooling time to any lower temperature. In the case of hypoeutectoid steels, the transformation of austenite to proeutectoid ferrite must be treated as a separate reaction having a higher equilibrium temperature (Ae_3). It is therefore necessary, when estimating cooling transformation from an isothermal diagram showing a ferrite beginning line, to plot the cooling curve as beginning at the Ae_3 temperature as well as at the Ae_1; the progress of transformation of austenite to proeutectoid ferrite is then determined as was done for that to pearlite in Fig. 8. If transformation during cooling is to be estimated accurately from isothermal data and then applied to actual heat treating, cooling should always commence at the same austenitizing temperature as was used in the determination of the isothermal diagram, and the austenitizing treatment prior to cooling should produce substantially the same austenite grain size; any difference in austenite grain size between the steel specimens used for the cooling study and those from which the isothermal diagram was determined will introduce an error which, for large differences in grain size, will be serious in the Ar′ region.

It is obviously possible, after determining, as outlined above, the progress of transformation for a sufficient number of different constant cooling rates, to construct a cooling diagram for the steel by drawing lines through the points on the several rate curves where transformation began or ended. For certain cooling rates, and particularly in the case of an alloy steel like S.A.E. 4340, the transformation may be more complex than that represented in Fig. 8; but the principles are still the same, and, bearing in mind the basic assumptions, it is possible to estimate the progress of cooling transformation in any given case. Nor is it essential that the method be

restricted to constant rates of cooling; it can be applied just as easily to any cooling provided the cooling history is well enough known to permit an accurate plot of the cooling curve on the isothermal diagram.

Discussion of Some Features of Austenite Decomposition Which Make it Possible to Estimate the Progress of Transformation on Cooling from the Isothermal Diagram

The assumptions regarding austenite decomposition, on which the proposed method for relating cooling transformation to isothermal data is based, are justified principally by the fact that the method has been applied to several grades of low alloy steel and found to check satisfactorily with direct experimental observations. As a further check, additional experimental studies were made in an attempt to determine the extent of the error involved in the method outlined above, particularly that resulting from the assumption that, in general, only a negligible amount of reaction occurs during cooling to the point of intersection of the cooling curve and the isothermal beginning line.

Transformation during continuous cooling for a given time period may be regarded as identical to that produced by an infinite number of consecutive isothermal transformation treatments at successively lower temperature levels, lasting, in the aggregate, the same total time. This suggested the use of "multiple" isothermal treatments as a means of approximating the behavior of austenite during cooling, and several grades of low alloy steels were studied experimentally in this way. Specimens rendered austenitic by a suitable heating were partially transformed at one temperature, then quenched into a second and, in some instances, a third constant temperature bath, and held for predetermined periods. The influence of the previous treatment upon the progress of transformation at the final temperature level was studied by microscopic examination after quenching to room temperature in the usual way. Such studies indicated that partial transformation at one temperature shortens the time necessary for austenite to begin to transform at a different temperature level, but that the character of the product and the rate of the reaction at a corresponding stage of the transformation is not noticeably affected by the previous partial transformation. An exception to this general conclusion was encountered, however, when the

rejection of proeutectoid ferrite during the initial holding period had considerably altered the composition of the residual austenite; this is a matter of little practical importance in deriving the Ar′ region of a cooling diagram, but must be taken into account when dealing with the bainite region of a derived diagram for a hypoeutectoid steel.

No visible change occurs in austenite held for any time interval shorter than that shown by the beginning line of the isothermal diagram; consequently it is not possible by direct measurement to determine the rate of reaction prior to the formation of a measurable amount of transformation product. It is probable that at least during most of this preliminary stage the first few stable nuclei of the new phase are simply growing to a visible size; from this standpoint, the reaction curve might logically be extrapolated beyond the visible beginning to zero time, and the amount of reaction at any instant prior to visible transformation would hence be some function of elapsed time. Mehl (9) and Avrami (10), (11) have presented mathematical analyses of austenite transformation dealing with, among other things, the kinetics of this preliminary stage in the reaction. The time period to the left of the beginning line of the isothermal diagram is always very short as compared to the time between the beginning and ending lines; from a practical standpoint, therefore, precise knowledge concerning the rate of reaction prior to visible transformation is not essential. The amount of reaction that has occurred during cooling to point "X" (Fig. 8) might be approximated experimentally by an isothermal treatment at the mean temperature of the cooling range (Ae_1 to T_X) for a holding period equal to the total time spent in cooling through this range. This was not done in the case of the 0.85 per cent carbon steel, but an analogous isothermal treatment was given to specimens of several grades of low alloy steel; judging from these experimental results, the amount of transformation on cooling to X in Fig. 8, if measured by the effect of such a treatment upon subsequent transformation at a different temperature, would be no more than would occur in a small fraction of the time necessary to produce visible transformation at the constant temperature T_X. Steinberg (7) and Hoyt (8) have proposed methods for evaluating the amount of reaction resulting from the cooling to any point such as "X"; their methods when applied to the present instance bear out the experimental contention that the fraction of reaction occurring during cooling at a constant rate to point "X" is small and can, in

practice, be neglected entirely without introducing serious error into the estimated beginning and ending of cooling transformation. In actual heat treatment, cooling usually occurs at a diminishing rate and the amount of transformation that would take place during cooling to the point of intersection of the cooling curve and the isothermal beginning line would, on the basis of either Steinberg's or Hoyt's methods, be even less than if the cooling had occurred at a constant rate.

The basic assumptions in the method proposed for relating transformation during cooling to the isothermal diagram are obviously approximations made in the interest of convenience and simplicity; any estimation of the temperature at which cooling transformation begins or ends is therefore incorrect to some extent. Present knowledge of the kinetics of austenite decomposition is inadequate to permit a precise determination of the magnitude of the error; in any case, it seems to be so small that it is unimportant from a practical standpoint, particularly when dealing with commercial grades of steel. There is reason to believe that the precise relation between cooling transformation and isothermal data will some day be evaluated, but for the present, a simple, approximate method for relating the two is considered sufficient for practical applications.

Derived Cooling Diagram for Plain Carbon Eutectoid Steel

The transformation of austenite, either at constant temperature or on continuous cooling is relatively complex in S.A.E. 4340 steel (Figs. 3 and 6) and may be of little interest to many who, however, are well acquainted with transformation phenomena in plain carbon steel. Consequently, it was considered worth while to include a cooling transformation diagram derived from the familiar isothermal diagram for plain carbon eutectoid steel.

On an earlier page, in discussing the schematic cooling diagram (Fig. 1) for 0.85 per cent carbon steel, it was pointed out that a more complete cooling diagram would result if a line showing the end of cooling transformation were included; such a diagram, derived from the isothermal diagram and shown in Fig. 9, represents transformation behavior during cooling at any constant rate. Obviously, in practice, a strictly constant rate is not likely to be encountered; the diagram is not, therefore, to be indiscriminately applied to actual

heat treatments, but is intended to show the fundamental pattern of cooling transformation in a plain carbon steel and how it is related to constant temperature transformation.

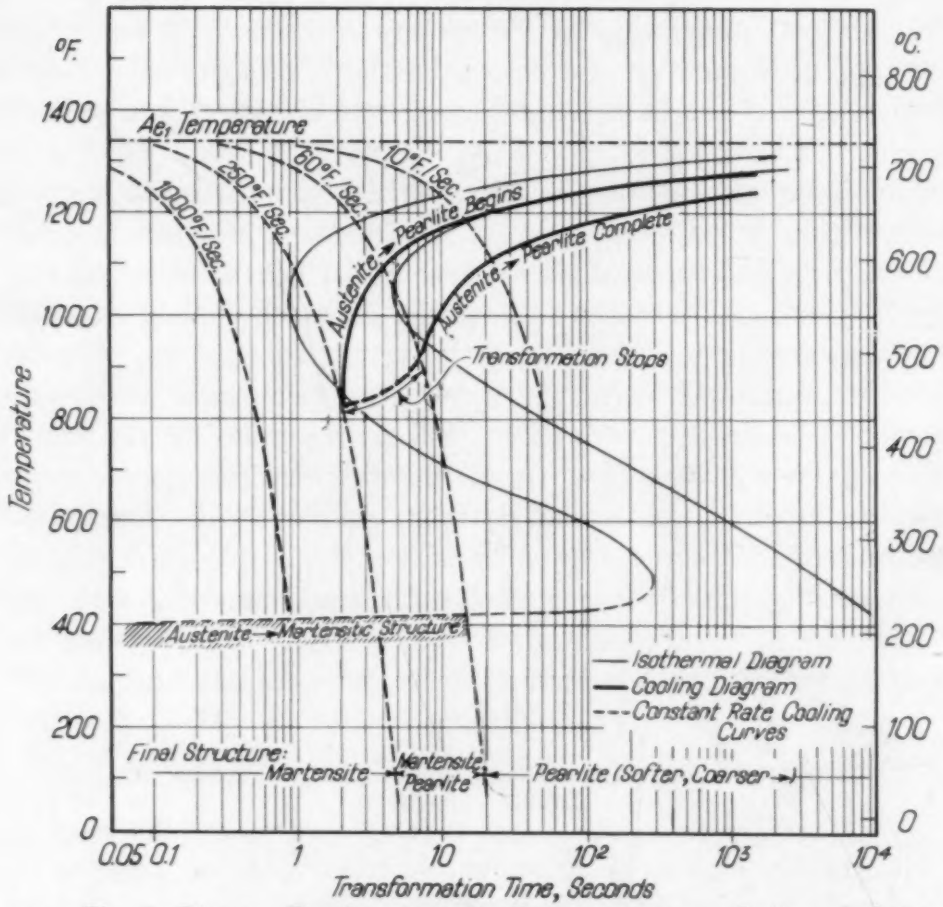

Fig. 9—Diagram Showing Austenite Transformation on Cooling at Constant Rate in a Plain Carbon Eutectoid Steel. Derived from the Isothermal Diagram.

Applications of the Isothermal Transformation Diagram to Heat Treating

The usefulness of steel as an engineering material is due largely to the fact that its structure and mechanical properties can be varied so greatly by heat treatment. The isothermal transformation diagram serves as a kind of map to guide the metallurgist in his search for the optimum structure and properties in a given steel. However, it is only by recognizing and evaluating the relation of cooling transformation to the isothermal diagram that he can make full use of the fundamental information given by the isothermal diagram.

Before use can be made of isothermal data as a basis for esti-

mating the amount of transformation on cooling, it is essential that the cooling history of the austenite prior to and during transformation be known or capable of close approximation. It is relatively easy to determine a cooling curve experimentally when the cooling is slow, but if the steel is quenched, or even air-cooled in small sizes, this is usually difficult and necessitates the use of special temperature-recording instruments. A number of researches have been made dealing with cooling rates during rapid cooling; those of French (12), in particular, may be mentioned as useful in approximating the cooling curve when direct experimental data are lacking. In practice, the important consideration is the time interval between the equilibrium transformation temperature and that of the so-called "nose" of the isothermal diagram. If this is known, it is possible to estimate the progress of transformation during the cooling, with what may often be satisfactory precision, by plotting the constant rate curve determined by this cooling time interval on the isothermal diagram and then applying the method previously described for relating transformation during cooling to the isothermal diagram. In an approximation of this kind, the greatest error arises from the fact that, owing to the heat evolution accompanying transformation, the actual cooling over the range of temperature at which the reaction occurred may not be sufficiently approximated by a constant rate of cooling.

Many practical applications of the method proposed for relating cooling transformation to the isothermal diagram will doubtless occur to the reader. As more isothermal diagrams and more precise data on cooling rates during actual heat treatments (quenching, welding, etc.) become available, its usefulness and the number of specific applications will be increased. Aborn (13) in a current paper has applied the derived relationship of cooling transformation to the isothermal diagram, in a simplified form, to the determination of the relative weldability of a steel. Other applications have to do with hardening and the development of desired properties by controlled cooling.

Hardenability and the Isothermal Diagram

Comparison of isothermal diagrams is a means of determining the ease with which steels may be hardened; this suggests the application of the relation of cooling transformation to the isothermal diagram for developing a more quantitative, but equally fundamental,

hardenability rating. Hardenability has been the subject of a great deal of discussion and it may be of interest to consider a simple method for rating hardenability directly from the isothermal diagram.

The "critical quenching rate" (see Fig. 1) is the slowest cooling that will produce a fully martensitic structure and has long been regarded as a means of rating hardenability. If it is to be a fundamental measure of hardenability independent of quenching variables,

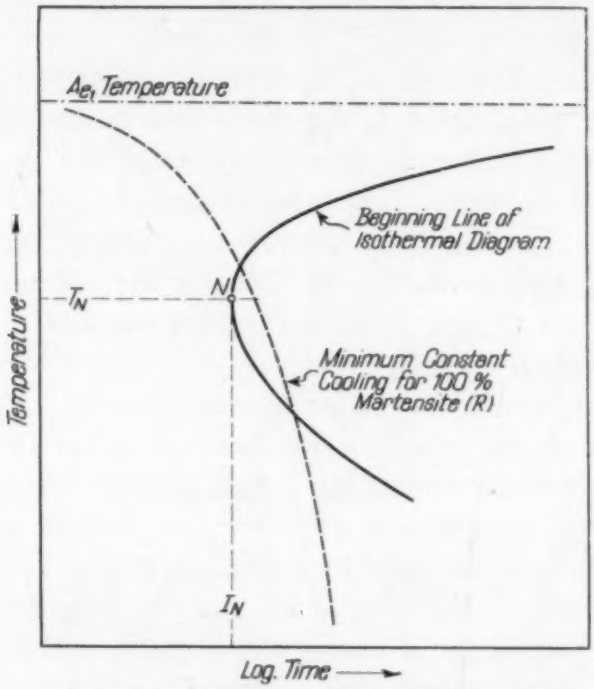

Fig. 10—Schematic Chart Showing the Manner in Which the Critical Constant Cooling Rate Intercepts the "Nose" of the Isothermal Transformation Diagram.

it is necessary to assume some uniform, hypothetical type of cooling. In the present instance, let us define the critical quenching rate as equivalent to the minimum constant rate of cooling that will produce, on cooling from the austenitizing temperature to room temperature, a fully martensitic structure.

With reference to the isothermal diagram, a curve representing this critical constant rate of cooling will intercept a portion of the "nose" of the isothermal diagram (see Fig. 10) and can be estimated by the method proposed for relating cooling transformation to the isothermal diagram. In numerous instances where this was done, it was found that the critical constant cooling rate could be simply approximated directly from the isothermal diagram as follows.

1. Locate point N (Fig. 10) at the "nose" of the beginning line of the isothermal diagram, that is, at the temperature and time where the beginning of transformation is most rapid.
2. Calculate the critical constant rate (R) by substitution in the empirical formula,

$$R = \frac{Ae - T_N}{1.5\ I_N}$$

where Ae = equilibrium transformation temperature (Ae_3 when N is on the ferrite beginning line, Ae_1 otherwise)
T_N = temperature at point N
I_N = time interval at point N

The factor 1.5 is based upon the observation that the time interval for cooling from the equilibrium temperature to T_N at the critical constant rate is approximately 50 per cent greater than I_N. Values of R for several steels calculated on this basis are listed in Table II; the isothermal diagrams used for determining N are those published by Davenport (2).

Table II
The Critical Constant Cooling Rate and Relative Hardenability of Several Grades of Steel as Computed from the Isothermal Diagram

Grade	Ae (Degrees Fahr.)	T_N (Degrees Fahr.)	I_N (Seconds)	$R = \frac{Ae - T_N}{1.5\ I_N}$ (Degrees Fahr. Per Second)	Relative Order of Hardenability (Lowest Number = Highest Hardenability)
S.A.E. 4340	1300	850	13.5	23	1
S.A.E. 4140	1445	900	2.5	150	2
S.A.E. 6140	1440	925	2	170	3
S.A.E. 3140	1390	1050	1.2	190	4
S.A.E. 5140	1425	925	1.6	210	5
S.A.E. 4640	1395	900	1.5	220	6
0.89 per cent C 0.30 per cent Mn	1335	1050	0.8	240	7
S.A.E. T1335	1430	950	0.9	360	8
S.A.E. 2340	1350	900	0.7	430	9
0.54 per cent C 0.46 per cent Mn	1400	1050	0.5	470	10
1.13 per cent C 0.30 per cent Mn	1335	1050	0.4	480	11

The calculated value of the critical constant cooling rate R may be regarded as a fundamental index of hardenability, the greater being the value of R, the less the hardenability. In considering the relative hardenability ratings shown in Table II, it should be realized that they are based upon the cooling rate that produces a fully mar-

tensitic structure. The measured hardness of such a structure would, in all probability, be only slightly greater than a structure containing, in addition to martensite, about 5 to 10 per cent of other types of structure (ferrite, pearlite or bainite) which, for all practical purposes, may be considered fully hardened. On the other hand, the constant cooling rate required, in any given case, to produce a final structure containing only 90 to 95 per cent martensite would be very much less, and it is probable that these cooling rates might result in a different relative order of hardenability for the steels listed in Table II, and possibly an order more in accord with hardenability ratings based on actual hardness measurements. Grossmann (14) determines hardenability on the basis of a final structure containing only 50 per cent martensite and, in order to obtain relative hardenability ratings directly from the isothermal diagram in close agreement with those obtained from Grossmann's method, it would be necessary to calculate and compare the constant cooling rate that would produce, for each steel, a final structure consisting of 50 per cent martensite.

The chief objection to this method of judging hardenability lies in the fact that it is based on what is often the least accurately determined portion of the isothermal diagram, namely, the beginning line at the "nose"; this fact, however, serves to justify the use of the approximate empirical formula rather than a more precise method for estimating the critical constant cooling rate from the isothermal diagram.

The above discussion has been included primarily as a demonstration of the relation of the isothermal diagram to the critical quenching rate and hardenability and as a specific application of the principles of relating cooling transformation to the isothermal diagram.

Summary

The isothermal diagram shows the fundamental transformation behavior of austenite at constant temperature; most actual heat treatments involve transformation as it occurs during cooling through a range of temperatures. The isothermal diagram is not, therefore, directly applicable to cooling transformation but can be used provided the relationship between the two types of transformation can be evaluated.

The results of a systematic study of cooling transformation in

S.A.E. 4340 steel indicate that the transformation occurs over a temperature range in which transformation at any instant during the cooling corresponds to isothermal transformation at the same temperature. Cooling transformation is therefore related to isothermal transformation; the relationship can be predicted with sufficient accuracy for most practical purposes from the isothermal diagram by a method developed empirically from experimental observations.

A cooling transformation diagram analogous to the isothermal diagram can be derived from isothermal data or determined experimentally; it lies below and to the right of the corresponding isothermal diagram. The amount of the displacement, in general, increases with more rapid cooling up to the rate which just produces on cooling to room temperature a fully martensitic structure.

The derived relationship between transformation on cooling and isothermal transformation may be employed to advantage in actual heat treatments provided the cooling history is known; it may also be used for determining the rate of cooling necessary to achieve a desired final product and combination of mechanical properties. The transformation which occurs during hardening, welding or heat treating by any method of controlled cooling can be predicted from the isothermal diagram which aids in understanding and designing such heat treatments.

Further studies of cooling transformation are desirable and should lead to a more exact evaluation of the relation between cooling and isothermal transformation. The present paper has doubtless raised many controversial points; if it promotes greater interest in the fundamental study of austenite transformation, it will have served a useful purpose.

Acknowledgments

The authors gratefully acknowledge the contributions made to this paper by other members of the staff of the United States Steel Corporation Research Laboratory. The work was done under the supervision and guidance of E. S. Davenport and Dr. John Johnston, Director of Research, United States Steel Corporation. T. W. Merrill assisted in obtaining some of the experimental data. Dr. R. H. Aborn and J. R. Vilella aided the authors with constructive criticism and advice.

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DISCUSSION

Written Discussion: By Robert M. Parke, metallurgist, Climax Molybdenum Co. of Michigan, Detroit.

Messrs. Grange and Kiefer have developed a much needed relationship between the S-curve of a steel and the temperature at which that steel will transform when cooled at a known rate. That this relation is empirical will scarcely detract from its usefulness, and its simplicity makes it especially attractive.

Two assumptions were used to obtain the derived cooling diagram. It is, therefore, of some interest to consider the errors which these assumptions will produce.

The first assumption, "That the extent of transformation of the austenite at the instant it cools to the intersection point X is not substantially greater than it would have been if quenched instantly to T_x"; will cause an error which will increase with increase in the slope of the upper portion of the S-curve and with decrease in cooling rate.

Since the formation of nuclei during the time spent in cooling from the equilibrium critical to the temperature at the intersection of the cooling curve with the S-curve will not be completely arrested, the first assumption tends to give a derived curve too low in temperature and too late in time.

The second assumption, "That on cooling through a limited temperature range, for example, T_x to T_o, the amount of transformation is substantially equal to the amount indicated by the isothermal diagram at the mean temperature $\frac{1}{2}$ $(T_x + T_o)$ after a time interval $I_o - I_x$", is valid when the nucleation period is independent of temperature or is a function of the first power of the temperature. In general the nucleation period (of alloy steels especially) is related to the temperature in a more complicated manner.

The writer had at hand some cooling curves, with correlated microstructures, of an S.A.E. 4140 steel for which the S-curve also was available; and, although the S-curve was obtained with a solution temperature of 1550 degrees Fahr., while a solution temperature of 1750 degrees Fahr. was used to obtain the cooling curves, it seemed worth while to apply the new relationship, even though the effect of the difference in solution temperature could not be accounted for completely. It was found in this case that, while the error was in the direction of a derived curve too high and too late, nevertheless, sufficiently satisfactory agreement between the experimental data and the predicted critical cooling rate and temperature of transformation was obtained. It appears, therefore, that the errors considered here are either not significant or are to some extent self compensating.

Authors' Reply

The authors are indebted to Mr. Parke for his interesting and pertinent discussion; it is particularly gratifying to learn that he took the trouble to apply the empirical method proposed by the authors for estimating from the isothermal diagram (S-curve) the progress of transformation during cooling and found that it resulted in a "sufficiently satisfactory agreement" with his own experimental observations.

As stated in the paper, the two assumptions upon which the empirical method is based are approximations made in the interest of convenience and simplicity; Mr. Parke has briefly discussed what he considers to be the probable errors involved in these two assumptions. In a general way, we are inclined to agree with Mr. Parke's statements with respect to the possible errors involved in our simplifying assumptions, but wish to point out that the precise nature and magnitude of these errors probably cannot be determined

until the mechanism of austenite transformation is completely and exactly understood. When our empirical method is checked against direct experiment, we have thus far always found that it permits estimation of the progress of cooling transformation with sufficient accuracy for practical purposes.

Mr. Parke suggests that the errors involved in the empirical method are "to some extent self-compensating." Whether or not such is the case is a question of no great importance since these errors are apparently of insufficient magnitude, in view of the usual precision in isothermal and cooling curve data, to be significant.

INFLUENCE OF SILICON AND ALUMINUM ADDITIONS ON THE CONSTITUTIONAL DIAGRAM OF 4-6 CHROMIUM-MOLYBDENUM STEELS

By C. L. Clark and M. A. Bredig

Abstract

This paper considers the effect of silicon and aluminum additions on the constitutional diagram of 4-6 chromium-molybdenum steel. It is shown that, in steels of this type containing 0.55 per cent aluminum, the inner gamma loop is closed at approximately 1.40 per cent silicon; while in the presence of 1.25 per cent silicon, 0.65 per cent aluminum accomplishes this same result. From this it follows that the additive effect of these elements in eliminating the alpha to gamma transformation is not the same as that determined from carbon-free alloys.

The results also show that, in the presence of 0.12 to 0.14 per cent carbon, the mixed alpha plus gamma field, at the temperature of maximum gamma solubility, is several times as wide as the homogeneous gamma area, which is a fact not always fully recognized. It is further indicated that, on heating, the mixed alpha plus gamma field passes directly into a partial liquid state rather than into a homogeneous alpha condition.

These results are in agreement with those previously presented by one of the authors on 5.0 and 7.0 per cent chromium steel with varying amounts of silicon, molybdenum and vanadium.

WHILE the constitutional diagrams of the binary alloys of iron-chromium, of iron-silicon, of iron-molybdenum and of iron-aluminum are well established, especially for the iron-rich materials, little information is available for the more complex alloy systems, such as produced by the simultaneous presence of iron, chromium, silicon, molybdenum and aluminum. The system becomes even more complex when carbon is present.

Chromium, silicon, molybdenum and aluminum all belong to the

A paper presented before the Twenty-second Annual Convention of the Society held in Cleveland, October 21 to 25, 1940. Of the authors, C. L. Clark is research metallurgical engineer, The Timken Roller Bearing Company, Canton, Ohio, and M. A. Bredig is associated with Vanadium Corporation of America, formerly holder of a Graduate Fellowship at University of Michigan. Manuscript received June 14, 1940.

gamma-loop forming group of elements, with the respective amounts of each of these elements required to eliminate the alpha to gamma transformation being approximately 12.5 to 13.0, 2.0, 3.0 and 1.0 per cent, in the absence of carbon. With carbon present these amounts are greater, and increase with increasing carbon content. Manganese causes an effect similar to that of carbon, although not in the same proportions.

The question then arises as to whether or not elements of the gamma-loop forming type exert a strictly additive effect when they are present simultaneously in a given steel. Information of this type is becoming of greater importance in order that some means will be provided for indicating the structures to be expected in the intermediate alloy steels, such as are now being widely used in high temperature applications.

The present investigation was confined to steels of the 4-6 chromium-molybdenum type, to which varying amounts of silicon and aluminum had been added, since they are well established in the high temperature field. These two elements exert a beneficial influence on the oxidation and corrosion resistance of this type of steel.

Steels Investigated

The steels necessary for this investigation were made by the Steel and Tube Division of The Timken Roller Bearing Company. They were melted in 20-pound heats in a high frequency induction furnace and were forged to ¾ inch rods at 2250 degrees Fahr. (1232 degrees Cent.) with no work being done below 1600 degrees Fahr. (871 degrees Cent.). The bars were then normalized at 1700 degrees Fahr. (927 degrees Cent.) for 8 hours, to eliminate the forging effects and to establish a more uniform grain size, after which they were annealed at 1500 degrees Fahr. (816 degrees Cent.).

The chemical compositions of the steels are given in Table I, classified into two groups. In the first, all the elements except silicon were held constant and this was varied in approximately 0.25 per cent steps from 0.25 to 3.30 per cent and then increased to 5.00 per cent. In the second group the aluminum content was the variable, starting at 0.002 per cent and increasing in 0.25 per cent steps to 1.50 per cent. The aluminum content of the first series was of the order of 0.55 per cent, and the silicon content of the second series was approximately 1.30 per cent.

Table I
Chemical Composition of Steels of the 4-6 Cr-Mo Type with Varying Silicon and Aluminum Contents

Heat Number	Chemical Composition, Per Cent							
	C	Mn	P	S	Cr	Mo	Si	Al
Steels with Varying Silicon								
497	0.13	0.35	0.017	0.017	5.12	0.58	0.25	0.565
491	0.14	0.37	0.012	0.020	4.86	0.58	0.49	0.575
500	0.13	0.32	0.010	0.017	5.04	0.55	0.77	0.565
493	0.14	0.36	0.016	0.018	5.04	0.56	1.05	0.578
494	0.12	0.37	0.016	0.018	5.04	0.57	1.24	0.578
495	0.13	0.36	0.018	0.020	4.95	0.56	1.49	0.563
501	0.13	0.34	0.011	0.018	5.12	0.52	1.76	0.568
498	0.12	0.37	0.010	0.016	5.05	0.59	2.04	0.56
499	0.13	0.36	0.012	0.019	5.03	0.52	2.34	0.56
502	0.13	0.34	0.011	0.018	5.18	0.56	2.47	0.59
599	0.14	0.33	0.010	0.016	4.95	0.59	2.77	0.53
596	0.13	0.35	0.014	0.018	4.97	0.58	3.05	0.52
600	0.14	0.34	0.012	0.015	4.96	0.55	3.29	0.55
650	0.13	0.35	0.013	0.016	5.00	0.55	5.00	0.55
Steels with Varying Aluminum								
605	0.13	0.36	0.010	0.014	5.23	0.59	1.32	0.002
606	0.14	0.38	0.012	0.018	5.03	0.59	1.30	0.24
494	0.12	0.37	0.016	0.018	5.04	0.57	1.24	0.578
607	0.14	0.38	0.013	0.019	5.13	0.58	1.25	0.71
608	0.14	0.36	0.013	0.019	5.00	0.55	1.31	1.17
610	0.15	0.38	0.012	0.019	5.04	0.56	1.34	1.51

Except for those elements which were purposely varied, the compositions of these steels were in close agreement. The total range in carbon content was from 0.12 to 0.15 per cent and, with but one exception, from 0.12 to 0.14 per cent. Likewise the range in manganese was from 0.33 to 0.38 per cent, in molybdenum from 0.52 to 0.59 per cent, and in aluminum (in the first series) from 0.52 to 0.59 per cent. The range in chromium content was somewhat greater, being from 4.86 to 5.23 per cent, but the influence of this element on the gamma-loop forming characteristics is not as drastic as that of the others.

Results

The procedure involved in this study of the influence of the silicon and aluminum alloy additions on the constitutional diagram consisted of the determination of the critical ranges by heating and cooling curves, hardness determinations on specimens quenched from temperatures up to 2552 degrees Fahr. (1400 degrees Cent.), and by a metallographic examination of many of the quenched specimens.

Heating and Cooling Curves—The inverse-rate curve method was used for the determination of the transformation points, both in heating and cooling. The samples, ¾-inch diameter by 1-inch, were

heated in an electric furnace to 2462 degrees Fahr. (1350 degrees Cent.). The temperature was measured with a platinum, platinum-rhodium thermocouple. The rate of heating and cooling was such that 10 to 15 seconds were required for a change of 0.02 millivolts (3 degrees Cent.), as measured with a precision type portable potentiometer.

With this procedure, a critical point was found to exist in all the steels, both on heating and cooling, at temperatures which in general increased both with increasing silicon content and aluminum content. These results are included in Figs. 1 and 2 and a relatively

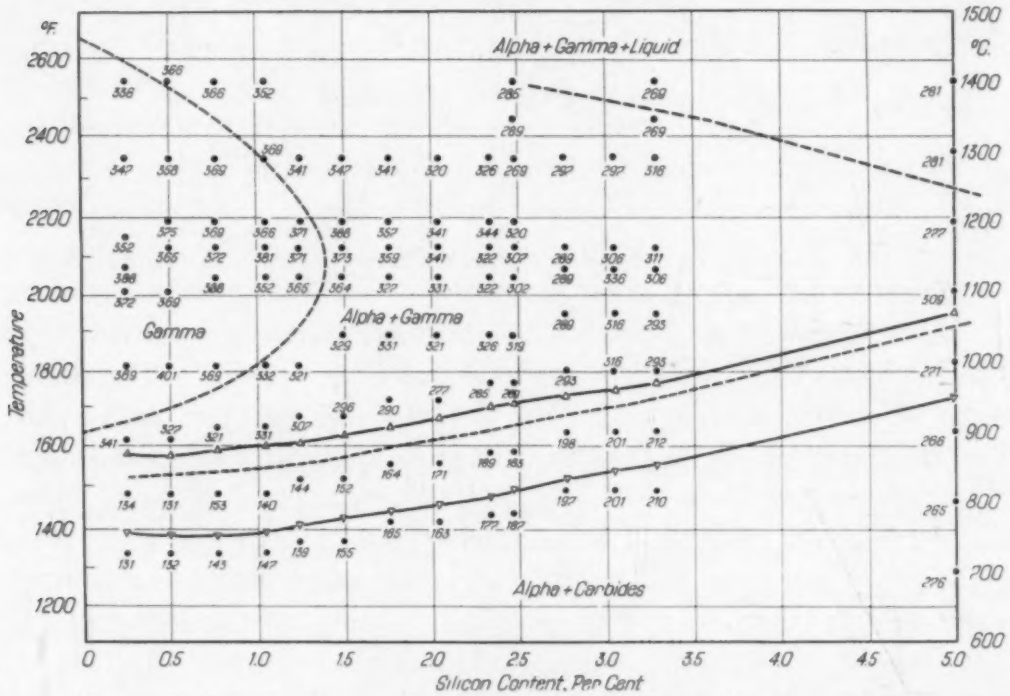

Fig. 1—Brinell Hardness of Quenched Specimens of 5.0 Per Cent Chromium, 0.55 Per Cent Molybdenum, 0.55 Per Cent Aluminum Steels with Varying Silicon Content.

large, but fairly consistent, difference of approximately 225 degrees Fahr. (125 degrees Cent.) exists between the A1 point on heating and cooling. This is believed to be due both to the heating and cooling rates employed and to the pronounced sluggishness of these types of steels.

The broken line of Fig. 1 extending from 1535 degrees Fahr. (835 degrees Cent.) for the 0.25 per cent silicon steel to 1920 degrees Fahr. (1050 degrees Cent.) for the 5.0 per cent silicon alloy is believed to be the approximate location of A1, based on the results from the heating and cooling curves together with the hardness de-

terminations and microstructures to be discussed later. For the sake of clarity only this single line is given in Fig. 2.

With the procedure employed critical points corresponding to the alpha plus gamma to gamma transformation were not obtained

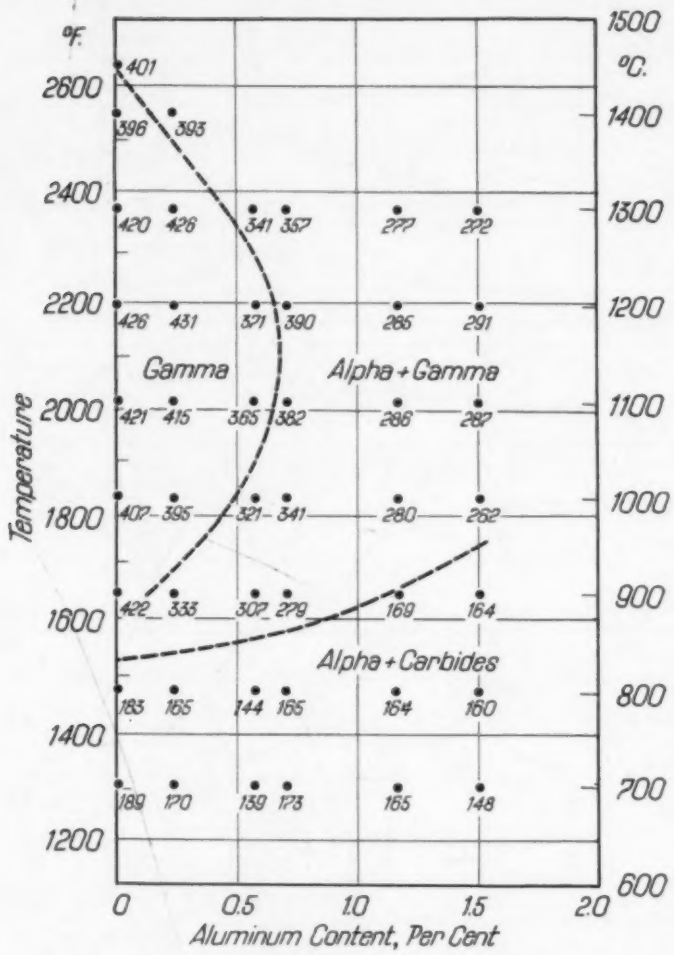

Fig. 2—Brinell Hardness of Quenched Specimens of 5.0 Per Cent Chromium, 0.55 Per Cent Molybdenum, 1.25 Per Cent Silicon Steels with Varying Aluminum Content.

either on heating or cooling. The reason for this was again believed to be largely due to the sluggishness in the transformation of these steels. For example, in the heating of the 0.75 per cent silicon steel, an appreciable amount of ferrite was transferred to austenite, after some superheating, inside the alpha plus gamma area, thus producing the pronounced thermal effect at 1607 degrees Fahr. (875 degrees Cent.). Further heating now caused immediate and continuous further transformation of ferrite at each temperature until the last ferrite had disappeared in reaching the lower boundary

of the austenite field. A thermal effect did not occur at the boundaries of the gamma loop.

Hardness Determinations: Sections ¾ inch diameter by ½ inch long heated in an electrical furnace for one hour, at temperatures ranging from 1292 degrees Fahr. (700 degrees Cent.) to 2552 de-

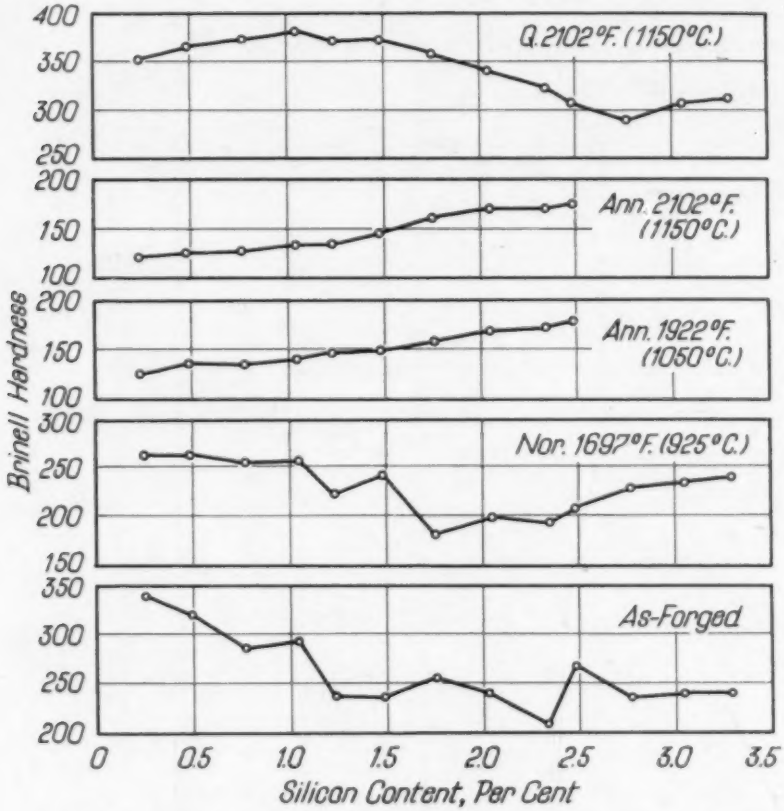

Fig. 3—Influence of Heat Treatment on the Hardness of 5.0 Per Cent Chromium, 0.55 Per Cent Molybdenum, 0.55 Per Cent Aluminum Steels with Varying Silicon Content.

grees Fahr. (1400 degrees Cent.), were quenched in a 4 per cent NaOH solution. The quenched bars were sliced to half cylinders, under cooling water, with a thin, rubber bonded, abrasive disk (wheel). The cut surfaces, representing the center of the specimens, were ground and one of these was used for hardness tests, the other for microscopic examination.

The results obtained from the hardness tests are likewise given in Figs. 1 and 2. As was to be expected an increase in hardness occurred as the A1 point was passed but the magnitude of this increase in hardness became less and less as silicon or aluminum contents increased. A further increase in hardness likewise occurred with both

series of steels in passing from the alpha plus gamma into the gamma loop with this second increase being of a lesser degree.

At those temperatures corresponding to the maximum extent of the closed gamma loop, the steels immediately beyond the loop had approximately the same hardness as those within. As will be shown later, this results from the fact that the amount of alpha iron present

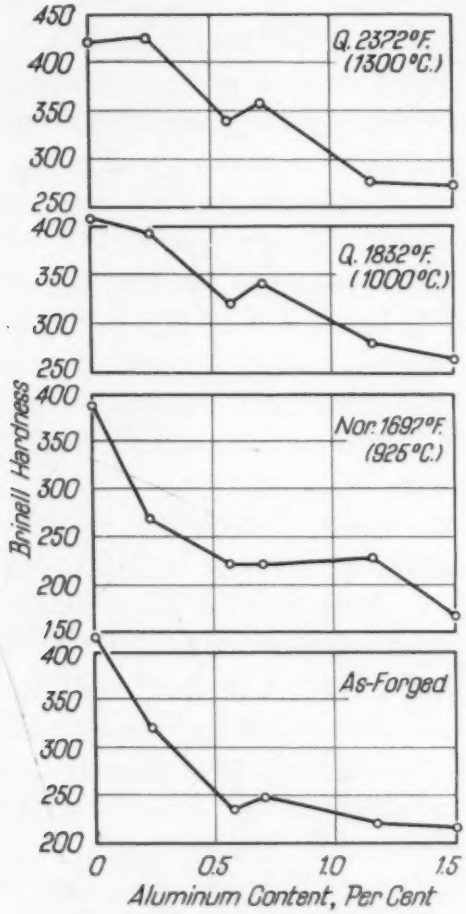

Fig. 4—Influence of Heat Treatment on the Hardness of 5.0 Per Cent Chromium, 0.55 Per Cent Molybdenum, 1.25 Per Cent Silicon Steels with Varying Aluminum Content.

is relatively small. In the silicon series, the maximum hardness remains above 300 Brinell up to 2.5 per cent silicon; while with the aluminum series the same is true up to 0.75 per cent aluminum. Likewise, no appreciable change in hardness occurs immediately upon passing above the gamma loop, that is, from the gamma to the alpha plus gamma region, and again this was due to the small amount of alpha iron present.

In order to better show the influence of increasing silicon or aluminum content on the resulting hardness of this 5.0 chromium —0.50 molybdenum steel, Figs. 3 and 4 are included in which hardness was plotted against the silicon content and the aluminum content, respectively. In the case of the aluminum series of steels, the hardness decreased continuously and rapidly with increasing aluminum content for each of the four treatments considered. With the silicon series, the hardness in the as-forged condition decreased with increasing silicon content while after quenching from 2102 degrees Fahr. (1150 degrees Cent.) or normalizing from 1697 degrees Fahr. (925 degrees Cent.), the hardness remained relatively constant up to 1.5 and 1.0 per cent silicon respectively after which it decreased and then again increased. However, annealing from either 1922 or 2102 degrees Fahr. (1050 or 1150 degrees Cent.) caused the hardness to increase slowly but continuously as the silicon is raised to 2.5 per cent.

Metallographic Examination: All of the quenched specimens from each of the steels were examined microscopically in order to determine the structural characteristics.

The extent of the inner gamma loop varies with temperature reaching a maximum at approximately 2100 degrees Fahr. (1150 degrees Cent.) with a silicon content of 1.40 per cent. However, at 1832 degrees Fahr. (1000 degrees Cent.) and 2372 degrees Fahr. (1300 degrees Cent.) the inner loop is closed at about 1.0 per cent silicon. It should be further noted that even though the silicon content was extended up to 5.0 per cent the outer boundary of the gamma loop was not closed although the trend of the data indicates that this closure would probably occur with around 6 to 7 per cent silicon. This, in turn, implies that at the point of maximum width the region between the inner and outer boundaries of the gamma loop, that is, the alpha plus gamma phase, is at least three times as wide as the inner gamma loop.

On the basis of this figure, this 4-6 chromium-molybdenum plus 0.55 aluminum cannot be placed in a single phase condition if the silicon content is in excess of 1.4 per cent, and the amount of alpha iron present will increase with increasing silicon content beyond 1.40 per cent. Likewise it cannot be made entirely ferritic unless the silicon content is greater than 5 per cent. Furthermore, at the temperatures more commonly employed in heat treatment, that is, 1550 to 1750 degrees Fahr. (843 to 954 degrees Cent.), a two-

phase structure results with a silicon content less than 1.4 per cent.

Likewise in the case of varying aluminum content in the 4-6 chromium-molybdenum plus 1.25 silicon steel the inner gamma loop is closed at 0.65 per cent aluminum with the maximum occurring at 2100 degrees Fahr. (1150 degrees Cent.). The further addition of aluminum to 1.50 per cent hardly begins to close the outer loop, thus again indicating the mixed phase of alpha plus gamma to occupy a considerably wider area than the homogeneous gamma phase. This implies that through the proper selection of temperature a single phase structure can be produced in this steel with aluminum contents up to 0.65 per cent but with aluminum in excess of this amount a two-phase structure exists.

Discussion of Results

While in the pure iron-aluminum, iron-silicon or iron-chromium diagrams both the gamma and the gamma plus alpha fields form loops, the present results indicate this condition to apply only to the homogeneous gamma field. At least in the varying silicon series of steels, the alpha plus gamma area is bordered at the higher temperatures not by the alpha field, but by a range in which liquid is one of the phases present. This fact is not to be ascribed to the combined influence of chromium, silicon, aluminum and molybdenum, but rather to the presence of 0.13 per cent carbon. This effect of carbon has already been shown by T. Murakami, K. Oka and S. Nishigori[1] in their constitutional diagrams of the iron-chromium-carbon system and is likewise to be observed in the iron-silicon-carbon system.[2]

In an attempt to determine if the elements considered are additive in their influence on the closing of the inner gamma loop, it will be seen that in the case of the silicon series, the loop was closed with approximately the following composition.

Carbon	Manganese	Chromium	Molybdenum	Aluminum	Silicon	
0.13	0.35	5.0	0.55	0.56	1.40	(a)

and in the aluminum series at about

Carbon	Manganese	Silicon	Chromium	Molybdenum	Aluminum	
0.13	0.35	1.25	5.0	0.55	0.65	(b)

[1] A. B. Kinzel and W. Crafts, "The Alloys of Iron and Chromium," Vol. I, p. 62, Fig. 34.

[2] E. S. Greiner, J. S. Marsh and B. Stoughton, "The Alloys of Iron and Silicon," p. 142, Fig. 69.

Neglecting for the present the carbon and manganese content, and considering the chromium, molybdenum, silicon and aluminum contents as being additive in the ratio of 1:4, 3:6, 5:13, then the equivalent chromium content for alloy (a) is 23.75 and for alloy (b) 23.92, and they are thus in close agreement.

If, as is sometimes done, a factor of 40 be applied to the carbon content and 2 to the manganese content and these amounts be subtracted from the equivalent chromium content then this value for alloy (a) becomes 17.85 and for alloy (b) 18.02. Both of these equivalent chromium content values are greatly in excess of the value of 13.0 per cent which is commonly recognized as the amount of chromium necessary to close the gamma loop in carbon-free steels.

Approaching this conversion in a somewhat different manner, the iron-silicon-carbon system is fairly well known and in the presence of 0.13 per cent carbon about twice as much silicon is required to close the inner loop as in carbon-free alloys. While as complete data are not available for the iron-molybdenum-carbon and iron-aluminum-carbon diagrams, it can be assumed that the influence of carbon is approximately the same, that is, that twice as much of each of these elements would be required with 0.13 per cent carbon as in the absence of carbon. On the basis of these assumptions, and making allowance for the influence of carbon on the iron-chromium diagrams, the ratio of chromium, molybdenum, silicon and aluminum required to close the loop would be 1:2, 5:3, 6:7.5 and the equivalent chromium content for alloy (a) becomes 15.6 and for alloy (b) 15.8.

Again these values are somewhat above those usually given as the amount of chromium required to close the inner gamma loop but when consideration is given to all of the variables involved and to the assumptions which were necessary, the agreement was good.

From this it must be concluded that, at least in the presence of 0.13 per cent carbon, the elements under consideration do not strictly exert the additive effect on the gamma loop indicated by the binary diagrams for carbon-free alloys. If this were the case then in the presence of 0.13 per cent carbon and 0.35 per cent manganese, the equivalent chromium content for closing the inner gamma loop would be approximately 23.8 and this is considerably above any reported value for straight chromium steels containing the same amounts of carbon and manganese. The apparent discrepancy is believed to be due to carbon exerting a greater influence on the binary systems of iron-silicon, iron-molybdenum and iron-aluminum than on the iron-

chromium system. Data are available to substantiate this in the case of the iron-silicon system but not in those of iron-molybdenum or iron-aluminum.

In a paper last year[3] the writers showed that at a heat treating temperature of 1750 degrees Fahr. (954 degrees Cent.), with steels containing 0.13 per cent carbon, 0.35 per cent manganese and with varying chromium, silicon, molybdenum and vanadium content, free ferrite, or delta iron, first appeared with an equivalent chromium content of about 19. In the present investigation the equivalent chromium content at this same temperature is 19.2 for the silicon series and 20 for the aluminum series. These findings are therefore in good agreement.

Conclusions

The results obtained from this investigation permit the following conclusions with respect to the influence of silicon and aluminum additions on the constitutional diagram of a 4-6 chromium-molybdenum steel containing 0.13 per cent carbon and 0.35 per cent manganese.

1. In the presence of 0.55 per cent aluminum, the inner gamma loop was closed at approximately 1.40 per cent silicon with the temperature of maximum gamma solubility being 2102 degrees Fahr. (1150 degrees Cent.). The outer gamma loop was not closed with 5.0 per cent silicon thus indicating that, at the temperature of maximum gamma solubility, the mixed field of alpha plus gamma was several times as wide as the homogeneous gamma field.

2. With a fixed silicon content of 1.25 per cent, the inner gamma loop was closed at 0.65 per cent aluminum with the temperature of maximum gamma solubility again occurring at 2102 degrees Fahr. (1150 degrees Cent.). The outer loop was not closed with 1.5 per cent aluminum and, as in the case of the silicon series, the mixed alpha plus gamma field appeared to be several times as wide as the gamma area.

3. The data further indicate that, on heating, the mixed alpha plus gamma field will not enter a homogeneous alpha field but will pass directly into a partial liquid state. This is in agreement with

[3] "Characteristics of 5.0 and 7.0 Per Cent Chromium Steels with Varying Molybdenum and Vanadium Content," Transactions, American Society for Metals, Vol. 27, No. 4, 1939, p. 1090-1117.

reported work on the iron-chromium-carbon and iron-silicon-carbon systems.

4. Assuming chromium, silicon, molybdenum and aluminum to exert a strictly additive effect on the closing of the inner gamma loop, in proportion to the ratios determined from their respective binary systems with iron, then the equivalent chromium content for the given carbon and manganese contents at the point of maximum gamma solubility, is 23.75 in the varying silicon series and 23.92 in the aluminum series. While these values are in close agreement with each other they are considerably greater than that for the straight chromium series with the same carbon and manganese content. This, in turn, implies that carbon exerts a greater influence on the silicon, molybdenum and aluminum diagrams than on the chromium system.

5. If it is assumed that 0.13 per cent carbon doubles the gamma solubility in the binary systems of iron-molybdenum and iron-aluminum, as is known to be approximately true in the iron-silicon system, then the equivalent chromium contents are 15.6 and 15.8 for the silicon and chromium series, respectively. These values are still somewhat higher than those generally accepted for the iron-chromium system.

6. For a temperature of 1750 degrees Fahr. (954 degrees Cent.) the results from this investigation are in agreement with that of work previously reported by the authors on 5.0 and 7.0 per cent chromium steels with varying amounts of silicon, molybdenum and vanadium in that the equivalent chromium contents, in the presence of 0.13 per cent carbon and 0.35 per cent manganese, are all of the order of 19.

ACKNOWLEDGMENTS

The authors wish to express their appreciation to officials of The Timken Roller Bearing Company for supplying the necessary steels and for their permission to publish the findings. Sincere appreciation is likewise given to J. W. Freeman, J. B. Urban, C. R. Levine, L. D. Orr and R. J. Herbenar for their assistance in various phases of the investigation.

DISCUSSION

Written Discussion: By R. H. Thielemann, research laboratory, General Electric Co., Schenectady, N. Y.

As the 4-6 per cent chromium-molybdenum steels, with silicon and alu-

minum additions, are finding such wide application in various types of high temperature equipment, this fundamental information reported by the authors is indeed timely.

The question of whether or not separate additions of the ferrite-forming elements, such as silicon, aluminum or molybdenum, to a 5 per cent chromium-iron alloy will have the same effect in rendering a closed gamma loop as would an equivalent addition of chromium, is difficult to answer. In the iron-chromium-carbon system, with carbon below 0.15 per cent and chromium not over 18 per cent, transformation reactions are more or less normal. However, with appreciable additions of silicon, molybdenum and aluminum, the knee of the S-curve is shifted to longer periods of time and the alloys become extremely air hardening. Reactions are sluggish and it is difficult to establish equilibrium conditions at the lower temperatures. Consequently very tiresome and exacting methods of study are usually required, and at best results are still difficult to interpret.

It seems that in order to establish a numerical chromium equivalent value for the outer limits of the closed gamma loop, accurate basic information must first be established. Although it is widely accepted that in the binary iron-chromium alloy, 13 per cent of chromium will render a closed gamma loop, the exact composition is still debatable. From investigations on alloys of high purity, Krivobok[4] has reported the presence of the gamma to alpha transformation even with alloys of 18 per cent chromium. Such an alloy would have a chromium equivalent value in excess of (+ 18) and this is even larger than the values of + 15.6 and + 15.8 reported by the authors for alloys (a) and (b) respectively. For most purposes, however, it seems that alloys having chromium equivalent compositions in excess of + 13 can be assumed to lie outside of the closed gamma field. Although these alloys are practically non-hardenable by the usual methods of heat treatment, there is reason to believe, as the authors have shown, that they are still within the ill defined limits of the two phase alpha + gamma region.

In working with alloys similar to the ones reported here the writer has found that the separate effects of the various alloying elements in narrowing or widening the limits of the gamma field in iron are, in most cases, cumulative. Thus, by adding together the individual chromium equivalent percentages of the various alloying elements present, it has been possible to calculate a chromium equivalent composition value for a given composition. Alloys of the same chromium equivalent composition are found to be similar, in many respects, to their position in the fields outlined by the closed gamma loop. Approximate chromium equivalent values for the various alloying elements in iron are given in Table I of this discussion.[5]

The authors point out that on heating, the mixed alpha plus gamma field will not enter a homogeneous alpha field, but will pass directly into a partial liquid state. They attribute this to the presence of carbon. The writer would

[4]V. N. Krivobok, Campbell Memorial Lecture, New York. October 3, 1934. (See page 25—The Book of Stainless Steels. Second Edition, American Society for Metals.)

[5]R. H. Thielemann, "Some Effects of Composition and Heat Treatment on the High Temperature Rupture Properties of Ferrous Alloys." Preprint No. 46 for 1940 Annual Meeting, American Society for Testing Materials.

Table I
Chromium Equivalent Values for Alloying Elements in Iron

Element	Lattice Type	Effect on Temperature Range of Gamma Phase[c]	Percentage by Weight to Eliminate Gamma Phase	Chromium Equivalent
Carbon	Amorphous	Widens	....	—40
Nickel	Face centered cubic	Widens	....	— 3
Manganese	Cubic	Widens	....	— 2
Copper	Face centered cubic	Widens	....	— 1
Cobalt	Hexagonal close packed	Widens (has weak effect)	....	.....
Chromium	Body centered cubic	Narrows	13	+ 1
Tungsten	Body centered cubic	Narrows	6	+ 2.1
Tantalum[a]	Body centered cubic	Narrows up to 1%	....	+ 2.8
Molybdenum	Body centered cubic	Narrows	3	+ 4.2
Columbium[b]	Body centered cubic	Narrows up to 1.8%	....	+ 4.5
Silicon	Cubic	Narrows	2.5	+ 5.2
Titanium	Body centered cubic	Narrows	1.8	+ 7.2
Vanadium	Body centered cubic	Narrows	1.2	+11.0
Aluminum	Face centered cubic	Narrows	1.1	+12.0

[a]Maximum solubility in alpha iron is about 1 per cent at 974 C. (1785 F.), see Metals Handbook, 1939 Edition, p. 359, American Society for Metals.
[b]Maximum solubility in alpha iron is about 1.8 per cent at 975 C. (1785 F.), see R. Genders, "Iron Niobium Alloys," *Engineering*, Vol. 148, November 3, 1939, p. 514 and 515.
[c]See E. C. Bain, "Alloying Elements in Steel," American Society for Metals, p. 9, 10, 11 (1939).

like to ask whether or not this partial liquid field will not also result from the addition of other elements which tend to widen the range of the gamma phase in iron.

From a practical standpoint, there is one factor in connection with the addition of appreciable amounts of silicon and aluminum to the 5 per cent chromium-molybdenum steel which is important. Although moderate additions are useful, sufficient amounts to place the alloy outside of the closed gamma field are not advisable if service at elevated temperatures is contemplated. The tendency for such alloys to become brittle with time at moderately elevated temperatures must not be overlooked. Also, if these alloys are to be welded, large grains and accompanying room temperature brittleness will develop during overheating. This condition can be relieved only by subsequent working of the welded metal.

Written Discussion: By A. J. Herzig, chief metallurgist, Climax Molybdenum Co. of Michigan, Detroit.

Before reading this paper it had not occurred to me that information on the effect of molybdenum on the gamma loop in iron-carbon-molybdenum alloys was not readily available in the literature. A paper by B. N. Svetchnikoff and N. S. Alferova, entitled, "The Alloys of the Iron-Carbon-Molybdenum System" (Theory and Practice of Metallurgy, Russia, 1936, No. 4, p. 72-83) includes this information, and I am presenting it in support of the authors' contention that twice as much molybdenum would be required with 0.13 per cent carbon as in the absence of carbon to close the gamma loop.

Several opportunities to check points on the diagram given in Fig. 1 indicate that these data are reasonably accurate.

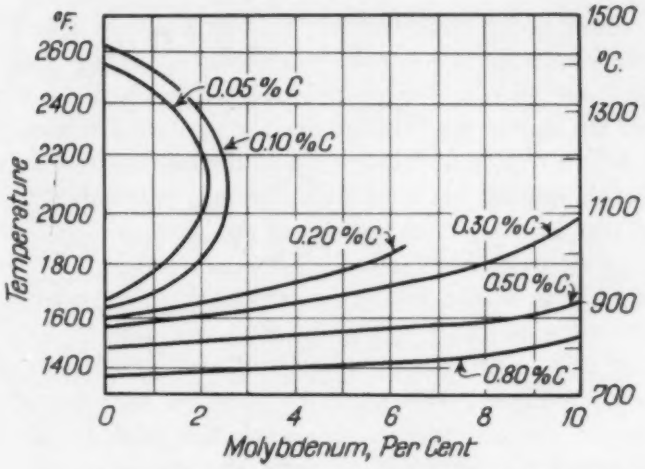

Fig. 1—The Effect of Molybdenum on the Gamma Loop in Iron-Carbon-Molybdenum Alloys.

Written Discussion: By W. O. Binder, Union Carbide and Carbon Research Laboratories, Inc., Niagara Falls, N. Y.

Specific data covering small portions of complex alloy steel systems, such as presented in this paper, are a distinct contribution to our knowledge of alloy steels. It is hoped that the authors will supplement these data with physical property data correlating the observed microstructures with high temperature strength and ductility and low temperature toughness, since these properties are strongly affected by the presence of ferrite[6] and variations in analysis.[7] Several photomicrographs illustrating the various structures observed would also be useful.

Oral Discussion

E. S. DAVENPORT:[8] I have one minor comment to make, almost in the nature of a quibble. I notice that the authors refer to the lower line in their Figs. 1 and 2, that is the line dividing the alpha plus carbide field from the alpha plus gamma field, as the A3: I would like to ask whether this line might not more properly be termed the A1? Is not the A3 usually considered to be the line which divides the 100 per cent gamma field from the alpha plus gamma field, reasoning by analogy from the iron-carbon diagram?

Authors' Reply

We appreciate the discussion which has been offered to this paper and wish to thank Mr. Herzig for calling to our attention the Russian work on the iron-molybdenum-carbon system. It is interesting to find that this confirms the assumption which was made in our own work.

With respect to the various questions raised by Mr. Thielemann, we agree

[6]W. G. Hildorf, C. L. Clark and A. E. White, "Characteristics of 5.0 and 7.0 Per Cent Chromium Steels with Varying Molybdenum and Vanadium Content," TRANSACTIONS, American Society for Metals, Vol. 27, 1939, p. 1090.

[7]Russell Franks, "Effects of Columbium and Other Addition Agents on Low Chromium Steels," TRANSACTIONS, American Society for Metals, Vol. 27, 1939, p. 78.

[8]Metallurgist, United States Steel Corp., Kearny, N. J.

that all of the alloys under consideration possess sluggish transformations and that equilibrium conditions were not established. In fact this was not the intention of the paper for we were primarily interested in ascertaining the structure present during hot fabrication, such as seamless tube piercing, as well as after normal commercial heat treatments. Information to date would indicate a fairly definite relationship between structure and pierceability.

It is agreed that in most cases an assumption that the ferrite-forming characteristics of these elements is cumulative would indicate the structures present. This would not be true in the borderline cases, at least under the procedures employed in this investigation.

In presenting this information, it was not our intention to recommend or imply that these two-phase steels should be used for high temperature service. The primary purpose for undertaking this work was to define the limits beyond which the steels would not be single phased. We do not agree, however, with the implication that two-phased or completely ferritic steels should never be used in high temperature applications. There are certain steels of this type which are rendering satisfactory service, especially in applications where oxidation and corrosion resistance are the prime requirements and strength and shock resistance are not important.

In reply to Mr. Davenport we agree that the line separating the alpha plus carbide region from the alpha plus gamma field should be designated as A1 rather than A3.

Work is in progress along the lines suggested by Mr. Binder and it is hoped sufficient data will soon be accumulated to permit definite correlations between physical properties and microstructures.

THE FATIGUE AND BENDING PROPERTIES OF COLD DRAWN STEEL WIRE

By H. J. Godfrey

Abstract

The paper presents the results of an investigation on the fatigue and bending properties of carbon steel wire. The special fatigue and bend testing machines developed for this study are described in this paper. The effect of wire drawing, decarburization and surface conditions on the fatigue properties have been investigated. The bend testing machine has been so designed that the severity of the bend test can be controlled in order to study the true bending properties of wire. Metallographic and X-ray studies of the internal structure of cold drawn wires are included in this paper.

Introduction

THIS investigation was primarily a study of the effect of cold working on the physical properties of steel wire. In this study the fatigue and bending properties as determined on especially designed testing machines have been emphasized.

Many investigators studying the wire rope problem feel that the most important stresses in a wire rope are those due to the repeated bending of the ropes when passing around sheaves and drums. This point of view has been challenged by others interested in this subject, since there are many factors other than actual stresses that help to determine the life of a wire rope. These factors include corrosion, abrasion, and localized compression forces on the surface of wire ropes and between the individual wires causing plastic flow to an extent which is generally not fully appreciated. However, the repeated bending stresses are important and a more complete knowledge of the fatigue properties of steel wire should lead to a *better* correlation between the manufacturing process of wire ropes with their service life.

The usual specifications for wire ropes include the tensile strength and the bending properties of the individual wires. Accord-

A paper presented before the Twenty-second Annual Convention of the Society held in Cleveland, October 21 to 25, 1940. The author, H. J. Godfrey, is engineer of tests, Fritz Engineering Laboratory, Lehigh University, Bethlehem, Pa. Manuscript received June 17, 1940.

ing to Bonzel (1),[1] the bend test is used in the mill to determine the malleability of wire. Bonzel states that under the present methods of bend testing it has been impossible to obtain an intelligent comparison between the results on a single wire in jaws of different radii of curvature. He also states that by varying the curvature of bending in accordance with some function of the wire diameter, it is impossible to get consistent results on wires in different stages of cold work. Many persons interested in the physical properties of rope wire give little credence to the bend test as it is now performed in the mill.

There are many factors affecting the bend test and since the conditions of testing have not been standardized there is little doubt as to the reason for the difficulty in interpreting the bend test results. In the design of the bend testing machine used in this investigation, as many unknowns as possible were eliminated.

The relationship between the bending and fatigue properties of steel wire is a debatable question. The bending of a wire around a small mandrel is very different than the conditions which exist in a fatigue test where the repeated bending stresses are in or slightly above the so-called elastic range of the material. However, in this study on the effect of wire drawing on the physical properties of steel, both the fatigue and bending properties show a definite change in their characteristics after a certain amount of cold working. It should be emphasized that the bend test cannot be substituted for the fatigue test. Prof. H. F. Moore stated in the 1939 A.S.T.M. Marburg Lecture (2) that no confidence should be placed in short time fatigue tests. In this instance the bend test is by no means a fatigue test and in no way may it be used to determine the actual fatigue properties of materials.

Von Ewald Buschmann (3) has attempted to determine the fatigue properties of materials by means of a bend testing machine similar to that described in this paper. The results of Buschmann's tests seem to be quite satisfactory for pure metals or alloys in the annealed condition in which the material is uniform throughout. However, this test would not be satisfactory for materials that are not uniform and whose fatigue properties are greatly affected by surface conditions.

Sachs and Sieglischmidt (4) report that as far as the effects of strength are concerned, the present information and tests show that

[1]The figures appearing in parentheses refer to the bibliography appended to this paper.

wires of a higher strength have a longer service life in spite of a correspondingly higher direct stress over the cross section. Since it has been found that for a given type of wire the fatigue limit stress increases in proportion to the tensile strength, it is quite logical that the endurance of a high strength wire rope operating around a given size sheave, will have a longer life than that of a lower strength rope around the same diameter sheave even though the actual direct stress in each case is a given percentage of the tensile strength of the wire. Sachs and Sieglischmidt also found that carbon steels had no direct relationship between the bend test and the strength properties as was found to be true for simple metals and other metallic alloys.

Wire Fatigue Machine

The two wire fatigue machines used in this study were designed and built at the Fritz Laboratory. The principle involved in the

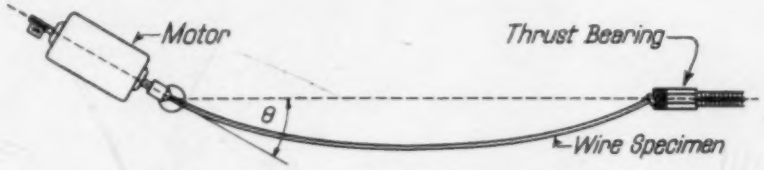

Fig. 1—Principle of Wire Fatigue Machine.

design of these machines is the same as that used in the Haigh-Robertson rotating wire fatigue machine which is now quite familiar to those interested in this subject. Changes were made, however, in several of the details which have simplified its construction without any loss in the required accuracy.

The difficulty encountered in the fatigue testing of wire is in stressing the wire specimen in such a manner that the test results are not affected by the gripping of the specimen. This difficulty is surmounted by stressing the wire specimen as a rotating wire strut, the ends of which are not fixed. Under this condition of loading the stresses vary from zero at the ends of the specimen to a maximum in the center of the column length. A diagrammatic view of the principle of the fatigue machine is shown in Fig. 1.

The stresses are computed by the well-known "Euler" column formula. The maximum stress at the center is equal to:

$$f = \frac{\pi^2}{360} \Theta \frac{d}{L} E$$

in which:

f = bending stress—pounds per square inch
Θ = inclination at the end of the wire—degrees
d = diameter of wire—inches
L = length of wire—inches
E = modulus of elasticity in tension—pounds per square inch.

The above formula is a close approximation and directly applicable when the angle of inclination is small. When the angle is greater than twenty degrees the curve of flexure changes perceptibly and a correction is necessary. However, for practically all fatigue tests made on steel wire the angle of inclination is less than twenty degrees.

A photograph of one of the wire fatigue machines is shown in Fig. 2. The machine consists of a base on which a motor is placed at one end and an adjustable tail stock at the other end. The wire specimen is held at one end by a chuck fitted to the shaft of the electric motor and by a thrust bearing at the other end. A special cap is fitted on the end of the wire which runs in the thrust bearing. In order to bend the wire to any desired angle of inclination an end thrust is applied by turning the tailstock. Simultaneously, the motor rotates the wire on its own axis, thus causing a complete reversal of the bending stress for each revolution.

The motor is placed in a swinging frame in such a position that the end of the chuck is exactly at the center of rotation of the frame. The counterweights on the swinging frame balance the weight of the motor. The angle of inclination is measured by a scale and vernier reading to 0.05 degrees, which for steel, corresponds to a stress of approximately 300 pounds per square inch for an L/d ratio of 150. When the specimen fractures, the swinging frame is thrown off balance and a mercury switch automatically stops the motor. The speed of testing used in these experiments was approximately 5000 revolutions per minute.

The stresses due to the dead weight of the specimen are not calculated as such, since the total stress is computed from the actual strains as measured by the angle of inclination. There is a small error caused by the fact that for a given stress at the center of the specimen the angle of inclination, due to the dead weight of the specimen, is not the same as that determined by the Euler formula. However, this difference is so small that it has no influence on the test results.

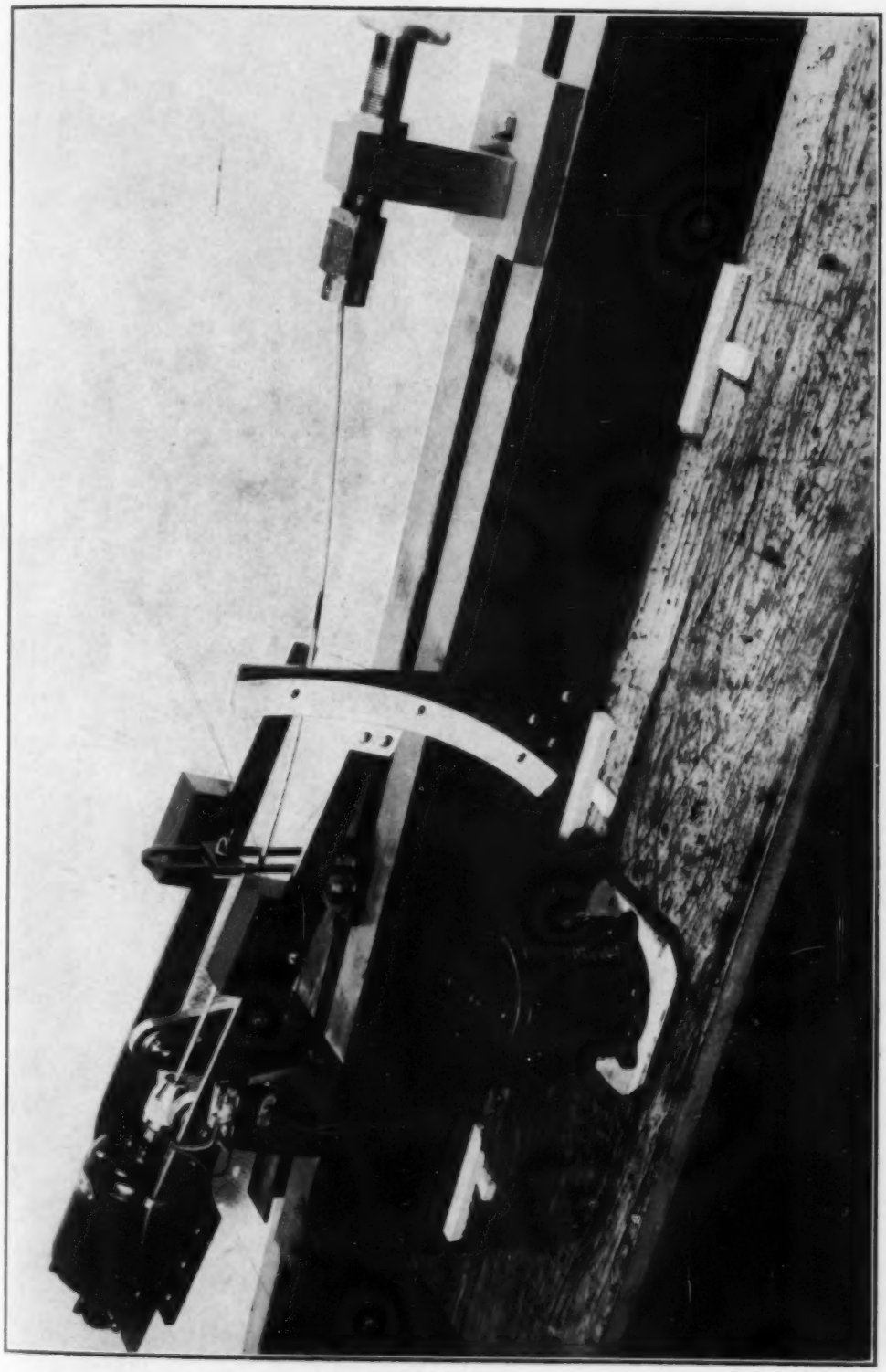

Fig. 2—Rotating Wire Strut Fatigue Machine.

Wire Bending Machine

The wire bending machine was designed and made in the Fritz Laboratory, and is shown diagrammatically in Fig. 3. A photograph of the bending machine is shown in Fig. 4. The wire is held in grips attached to the bending arm and weights are suspended at the

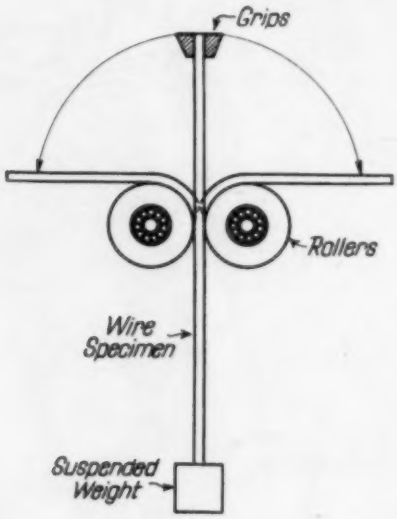

Fig. 3—Principle of Wire Bending Machine.

lower end of the wire. The wire is then bent back and forth over the rollers by moving the bending arm through an angle of 180 degrees. These rollers are supported on bearings so that they are free to rotate during the bending operation. The rollers can be adjusted so that the clearance between them is slightly more than the diameter of the wire. The center of rotation of the bending arm is at a point 0.7R above the center of the rolls, where R = the radius of the rollers. In this position there is very little vertical movement of the wire during the bend test. For the various sizes of rollers used the bending arm may be adjusted to the proper elevation.

The bending machine is operated by hand and the speed of testing of fifty 180-degree bends per minute is controlled by a Metronome. The direct tensile stress in the wire specimen, due to the suspended weights, is equal to one per cent of the tensile strength of the wire. Three or four specimens were tested to failure for each roll size and the average number of bends were used to compare the bending properties of the various materials.

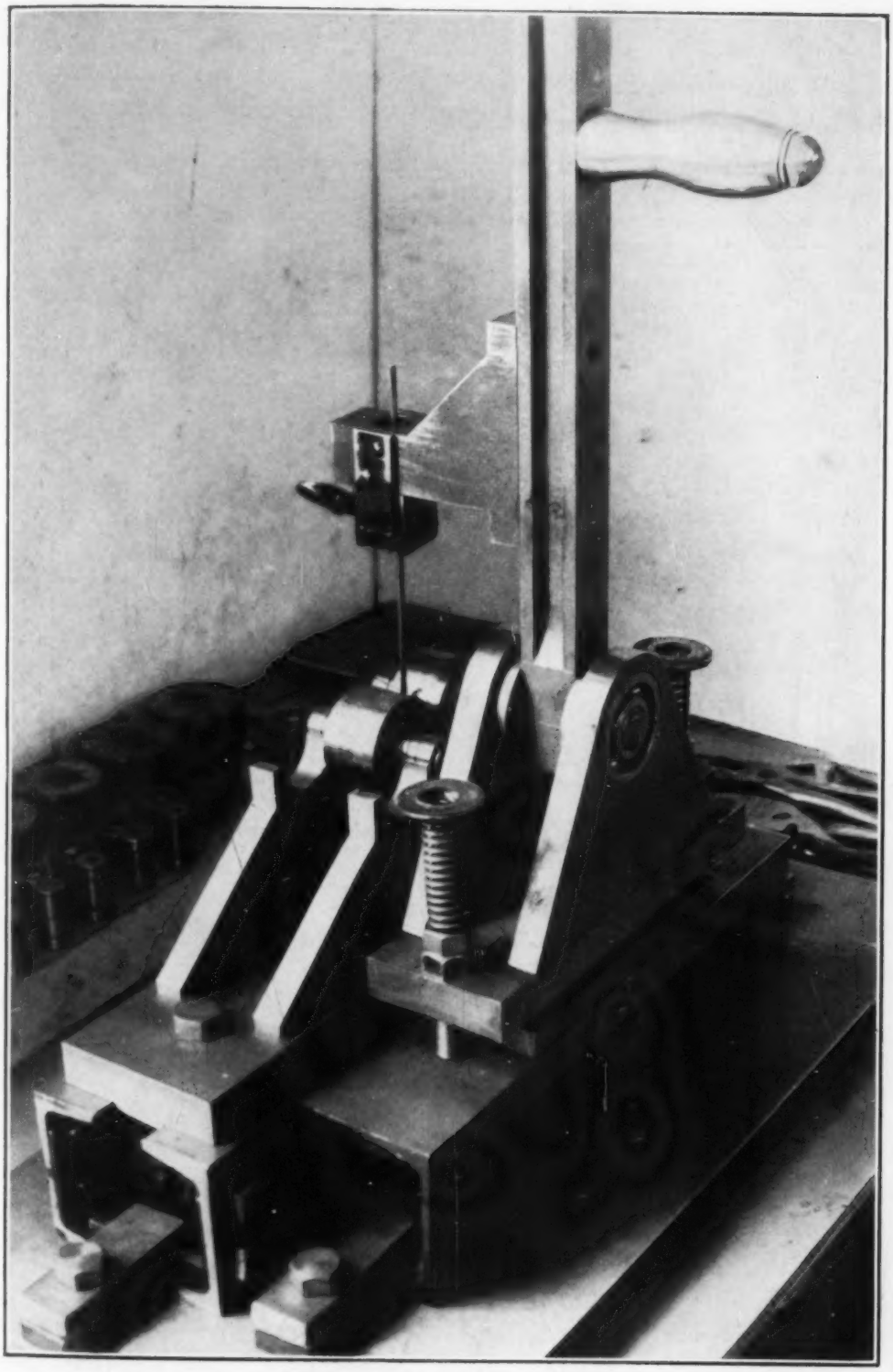

Fig. 4—Wire Bending Machine.

Materials

The physical properties of the materials included in this investigation on the fatigue and bending properties of cold drawn steel wire

Table I
Tensile and Fatigue Properties of Cold Drawn Steel Wire

Carbon Content Per Cent	Diameter In.	Per Cent* Reduction	Per Cent* Elongation	Tensile Strength P.s.i.	Elong. in 10 In. Per Cent	Fatigue Limit P.s.i.	Fatigue Ratio Per Cent
0.05	0.215	0	0	45,900	24.0	.....	....
0.05	0.134	61.2	157	75,500	4.4	36,000	47.6
0.05	0.112	73.0	269	84,000	3.2	39,300	46.8
0.05	0.062	91.7	1104	105,000	1.6	40,100	38.2
0.16	0.215	0	0	59,700	21.5	.....	....
0.16	0.135	60.5	154	92,000	3.7	39,600	43.0
0.16	0.112	73.0	269	101,400	3.25	42,000	41.4
0.16	0.062	91.7	1104	128,000	1.15	43,400	33.9
0.39	0.205	0	0	101,500	9.0	.....	....
0.39	0.136	56.0	127	135,000	4.6	47,000	34.8
0.39	0.113	69.6	229	148,000	4.3	55,800	37.7
0.39	0.062	91.0	994	208,000	1.6	60,400	29.0
0.58	0.139	0	0	144,500	9.5	45,200	31.2
0.58	0.106	41.9	72	171,500	6.1	55,800	32.5
0.58	0.081	65.9	195	195,000	5.6	63,500	32.5
0.58	0.061	80.6	418	227,000	2.9	64,500	28.4
0.90	0.147	0	0	212,000	7.5	68,200	32.2
0.90	0.124	28.8	41	222,000	6.8	72,500	32.6
0.90	0.102	51.9	108	239,000	5.9	79,000	33.0
0.90	0.085	66.6	199	258,500	4.4	83,600	32.4
0.90	0.077	72.6	264	272,000	3.8	90,000	33.1
			Polished Wire				
0.05	0.112	73.0	269	84,000	3.2	43,000	51.2
0.16	0.112	73.0	269	101,400	3.25	46,000	45.4
0.39	0.113	69.6	229	148,000	4.3	63,000	42.6
0.58	0.106	41.9	72	171,500	6.1	61,000	35.6
0.90	0.124	28.8	41	222,000	6.8	85,000	38.3

*By Wire Drawing.

are presented in Table I. This material was analyzed for its carbon and manganese content and the results are as follows:

Carbon Per Cent	Manganese Per Cent
0.05	0.11
0.16	0.49
0.39	0.75
0.58	0.60
0.90	0.35

The 0.05 and 0.16 per cent carbon wires were drawn from a hot-rolled green rod to the various wire sizes. The 0.39 per cent carbon material was drawn from a lead-patented rod and the high carbon material was drawn from wire which had been given an in-

termittent patenting. Although the exact temperatures of heat treatment were not available, it will suffice to say that the patenting process usually consists of quenching in lead to 900 to 950 degrees Fahr. (480 to 510 degrees Cent.) from above the critical temperature.

Table II
Tensile and Fatigue Properties of Decarburized Cold-Drawn Steel Wire

Material	Carbon Content Per Cent	Diameter—Inches—Net	Diameter—Inches—Gross	Per Cent* Reduction	Tensile Strength P.s.i.	Fatigue Limit P.s.i.	Fatigue Ratio Per Cent
Plain	0.73	0.095	.....	50.5	202,000	46,000	22.8
	0.73	0.085	.....	59.9	215,000	52,000	24.1
	0.73	0.074	.....	70.0	228,000	54,000	23.6
	0.73	0.060	.....	80.0	240,400	60,000	24.9
						Average	23.8
Electro-Galvanized Wire	0.73	0.1035	0.1065	48.1	185,000	47,000	25.4
	0.73	0.081	0.083	68.5	213,000	50,000	23.4
	0.73	0.070	0.072	76.4	236,000	54,000	22.9
	0.73	0.0585	0.060	83.5	243,000	58,000	23.9
						Average	23.9
Hot Galvanized Bridge Wire	....	0.190	0.194	....	235,000	48,000	20.4

*By Wire Drawing.
All Values Computed on the Net Diameter of Wire.

The material used in a supplementary study is presented in Table II. The chemical analysis of this wire is as follows:

	Carbon	Manganese	Phosphorus	Sulphur	Silicon
Bare Wire	0.73	0.65	0.028	0.025	0.19
Electro-Galvanized	0.73	0.56	0.026	0.025	0.18

The 0.73 per cent carbon material was lead-patented before drawing. The hot-galvanized wire included in Table II is cold-drawn bridge wire.

Discussion of Test Results

Metallographic Study—The metallographic examination of the material included in Table I was made to determine the structure of the rod before being drawn into wire and also to determine to what extent the surface of the material was decarburized. The photomicrographs of the 0.05, 0.16, 0.39, 0.58, and 0.90 per cent carbon material are presented in Fig. 5. The photomicrographs at one hundred magnification show that there is little or no decarburization on any of these materials. There were no further heat treatments on this material during the following stages of wire drawing.

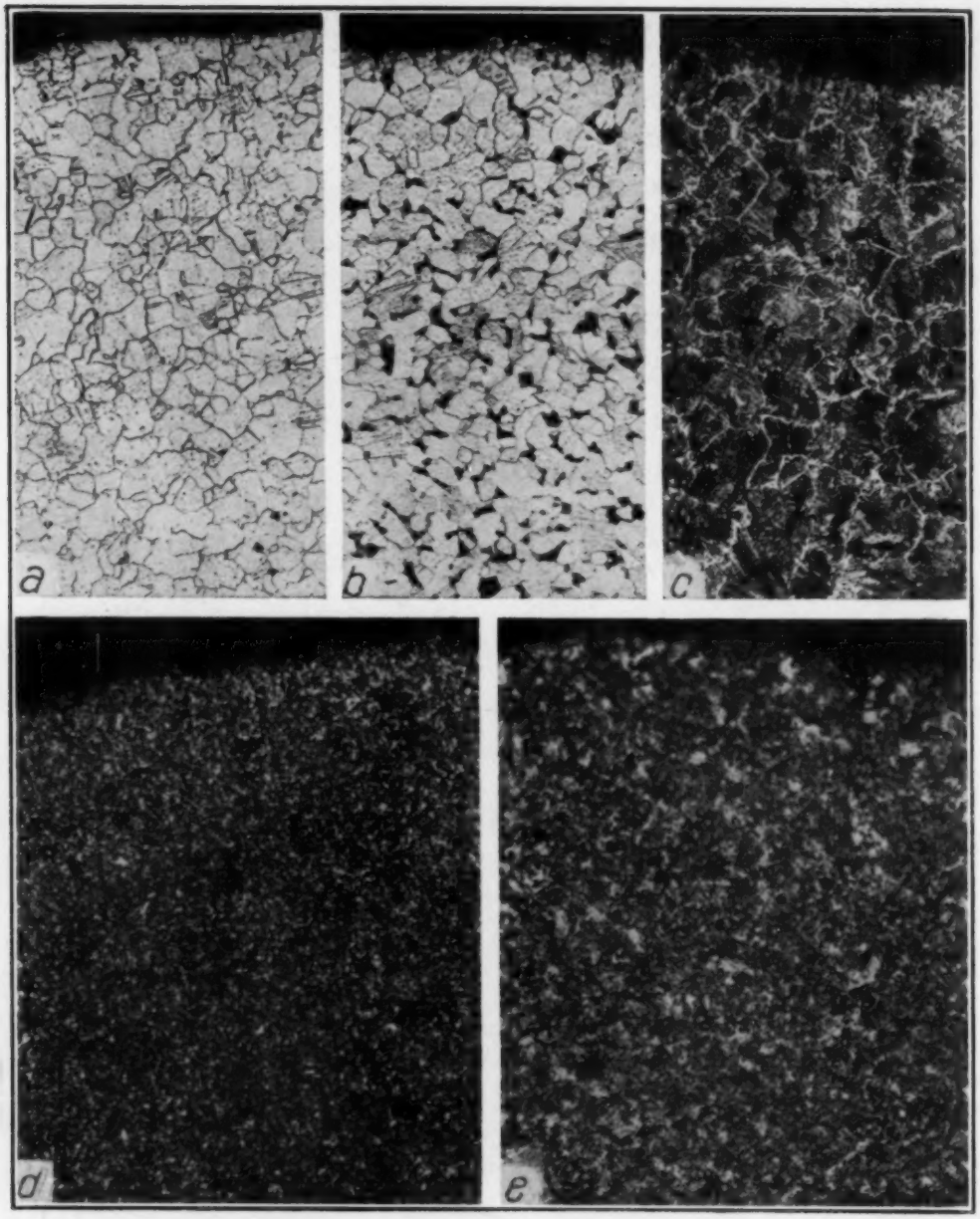

Fig. 5—Photomicrographs of Hot-Rolled and Patented Steel Rods. × 100. a.—0.05 Per Cent Carbon; b.—0.16 Per Cent Carbon; c.—0.39 Per Cent Carbon; d.—0.58 Per Cent Carbon; e.—0.90 Per Cent Carbon.

The 0.73 per cent carbon wire in Table II was included in this investigation in order to study the effect of decarburization on the fatigue properties of wire. The photomicrograph in Fig. 6 shows a distinct ring of decarburized material at the surface of the bare wire. Since the patented wire was not available for examination this photomicrograph was made from the 0.095-inch diameter wire drawn 50.5 per cent reduction. A study of the depth of decarburization was

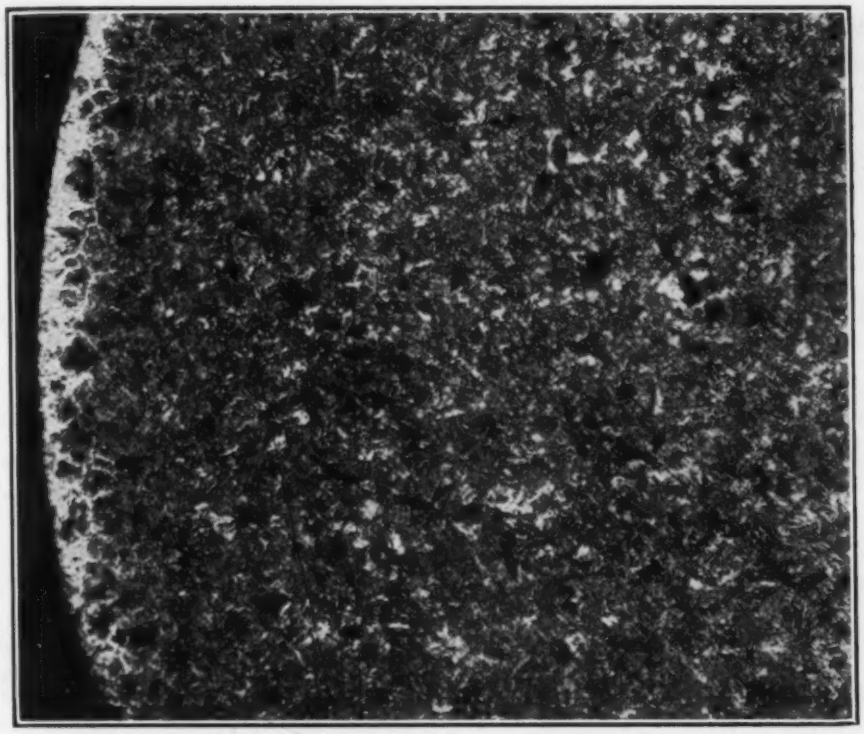

Fig. 6—Photomicrograph of Decarburized 0.73 Per Cent Carbon Steel Wire. × 100.

also made on the 0.73 per cent carbon electro-galvanized wire and the results were as follows:

Electro-Galvanized 0.73 Carbon Wire

Net Diameter, Inches	Decarburization, Inches	
	Maximum	Minimum
0.1035	0.011	0.005
0.0810	0.010	0.006
0.0700	0.009	0.007
0.0585	0.008	0.004

It should be noted that the amount of decarburization was about the same for both the bare and electro-galvanized 0.73 per cent carbon wire.

A metallographic study of the cold drawn hot-galvanized bridge wire also showed a distinct layer of decarburized material beneath the hot galvanized coating.

Tensile Properties—In a study on the effect of cold working on the properties of steel an expression for the amount of cold work should be formulated. In the manufacture of steel wire the amount of cold working by wire drawing is usually expressed by the per cent

reduction in area of the original rod or patented wire. This is expressed by the equation:

$$\text{Per cent Reduction} = 100 \times \frac{A_o - A_f}{A_o}$$

where A_o = original area

A_f = final area

Another means of expressing the amount of cold working is by the per cent elongation by wire drawing which is found as follows:

$$\text{Per cent Elongation} = 100 \times \frac{A_o - A_f}{A_f}$$

This expression shows the amount that the wire has been stretched

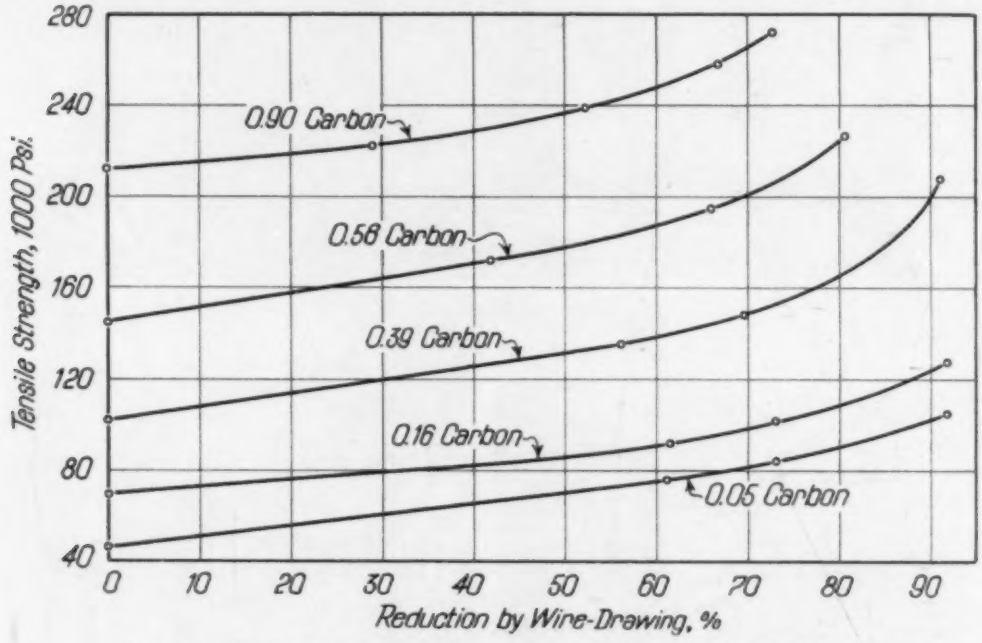

Fig. 7—Effect of Wire Drawing on Tensile Strength of Steel Wire.

or elongated by the wire drawing process. This value could reach infinity for a material with perfect ductility and often reaches as high as 3000 per cent. For example, an elongation of 1000 per cent means that the wire has been drawn eleven times its original length and is equal to 90.9 per cent reduction in the cross sectional area.

The relation between the tensile strength of steel wire and the per cent reduction by wire drawing and per cent elongation by wire drawing is shown in Figs. 7 and 8. From these two figures it appears that the amount of cold working is more logically expressed by the percentage elongation since in this case, the tensile strength increases at a greater rate at the initial stages of wire drawing, where-

as when related to the per cent reduction, the tensile strength increases at a more rapid rate during the final stages of wire drawing. However, since it is general practice to use the per cent reduction by wire drawing for comparative purposes, all other values in this report are compared on this basis.

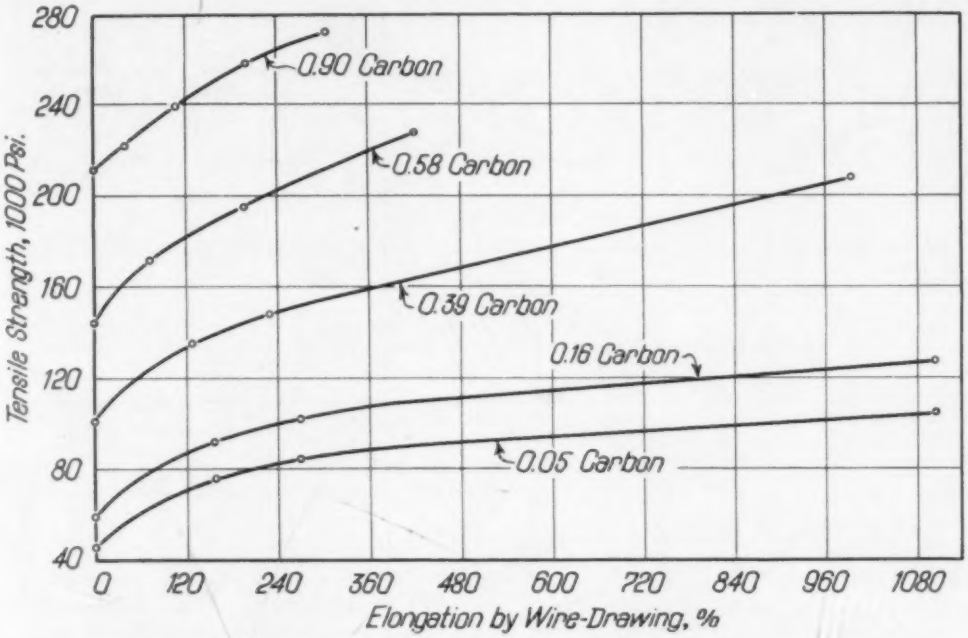

Fig. 8—Effect of Wire Drawing on Tensile Strength of Steel Wire.

Fatigue Properties—The fatigue properties for the wire free from decarburization are shown in Table I, along with the other physical properties as determined by the tensile test. This material was machine-straightened before any of the physical properties were determined. This straightening operation was performed so that a perfectly straight specimen could be used in the rotating wire strut fatigue machine. A number of tensile and fatigue tests were made on both machine and hand-straightened wire and it was found that the machine straightening process did not affect the test results to any appreciable amount.

The actual endurance curves for the carbon steels in Table I are presented in Figs. 9 to 13. These curves are presented mainly to show the effect of the carbon content on the characteristics of the fatigue curves. It should be noted that for stresses just above the fatigue limit the low carbon steels undergo a great many more cycles before fracturing than the high carbon steels. For example, a 0.05 per cent carbon wire fractured after nine million stress-cycles, where-

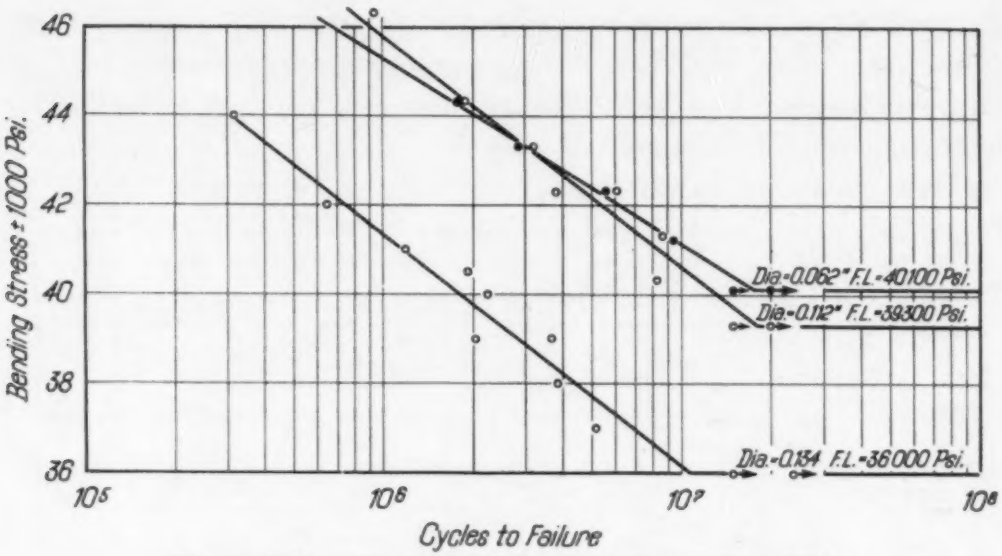

Fig. 9—Fatigue Test on 0.05 Per Cent Carbon Steel Wire.

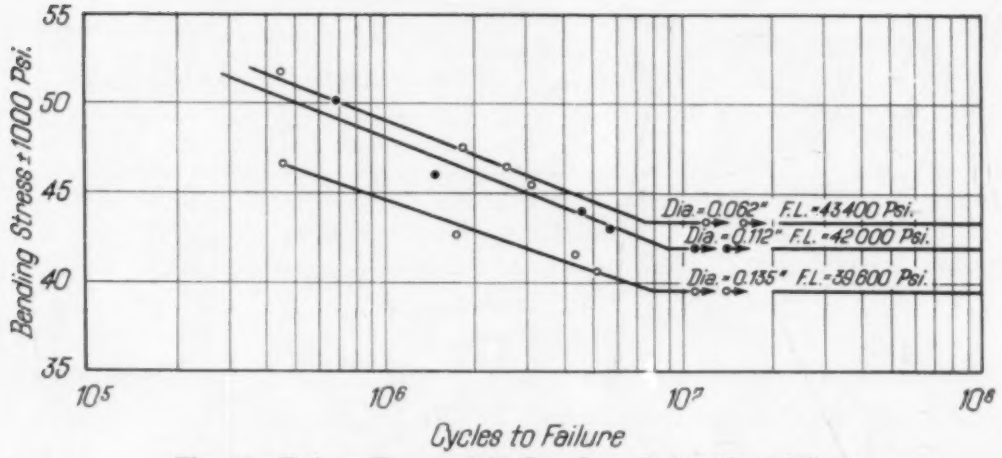

Fig. 10—Fatigue Test on 0.16 Per Cent Carbon Steel Wire.

as the maximum number of cycles before fracture for a 0.90 per cent carbon wire was slightly over one million cycles. The intermediate carbon steels ranged between these two limits. Gill and Goodacre (5) report that five million cycles were sufficient to indicate the fatigue limit of wire. Since their tests included only materials with a carbon content of over 0.36 per cent, their analysis was correct for the material investigated. However, the true fatigue limit for very low carbon steels should be determined from tests of over 10 million cycles in duration. Fractures in other metals such as aluminum take place after 100 million cycles of stress.

The effect of wire drawing on the fatigue properties of the material free from decarburization is presented in Fig. 14. These

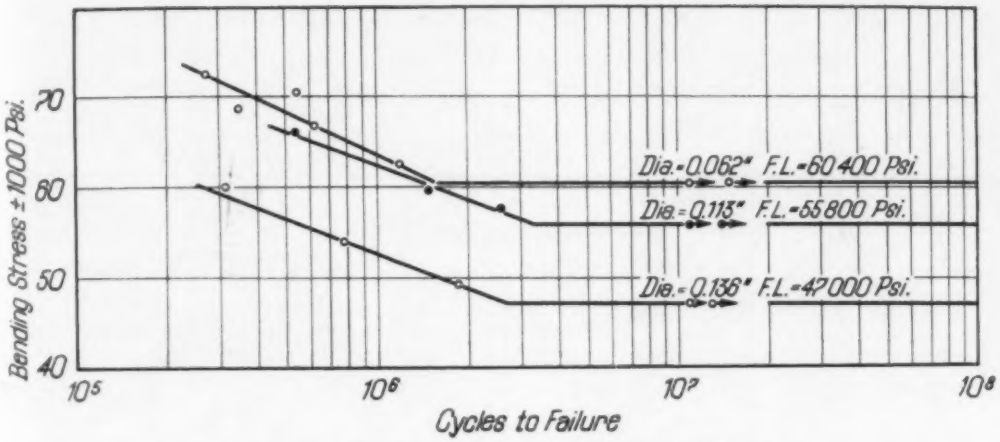

Fig. 11—Fatigue Test on 0.39 Per Cent Carbon Wire.

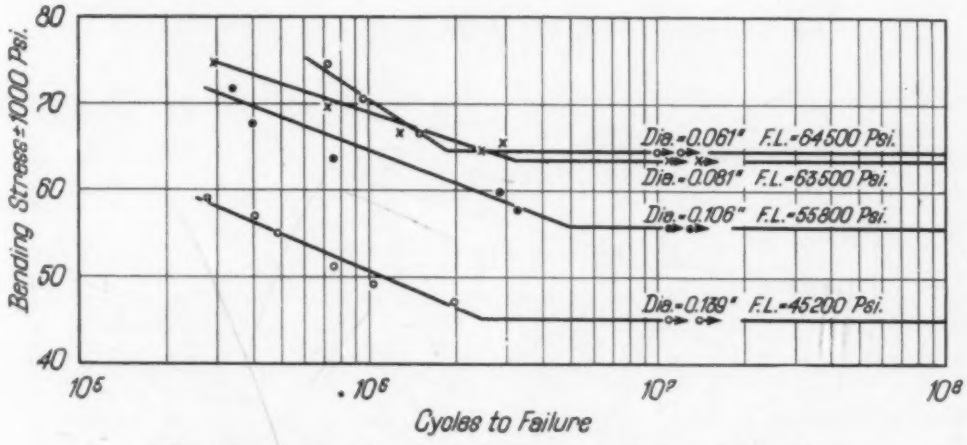

Fig. 12—Fatigue Test on 0.58 Per Cent Carbon Steel Wire.

curves show that the fatigue properties of steel wire increase with cold working, although the rate of increase is not always in proportion to the amount of wire drawing.

The relationship between the fatigue limit stress and the tensile strength of steel wire is of importance. The fatigue limits as compared to the tensile strength of the various carbon steels are shown in Fig. 15. On first sight it would appear that the fatigue limit is approximately a function of the tensile strength of the material regardless of the carbon content. However, when we note the ratio between the fatigue limit and the tensile strength as shown in the last column of Table I we find that this ratio (hereinafter termed the fatigue ratio) decreases with an increase in carbon content. This relationship is presented in Fig. 16. The solid line is an average for all the materials which have been wire drawn less than 75 per cent

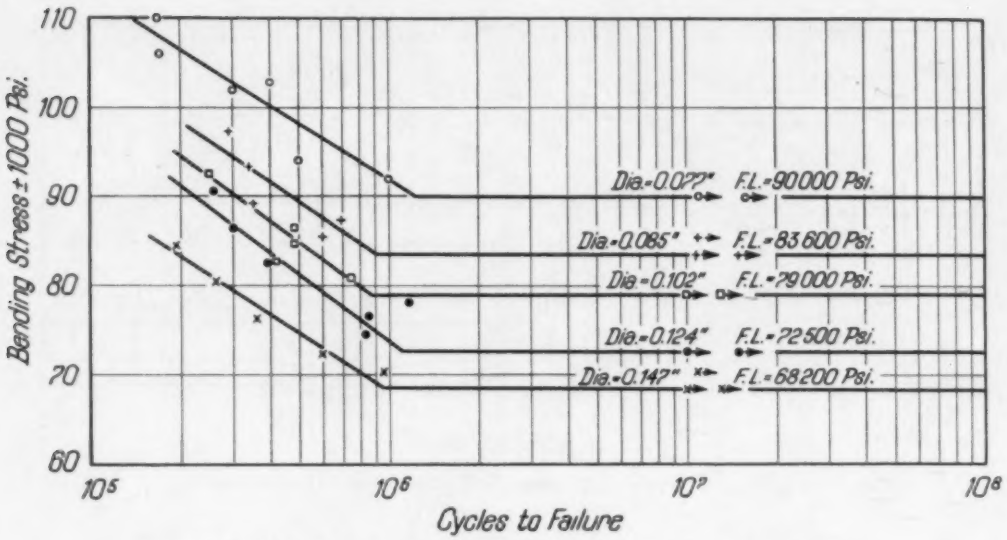

Fig. 13—Fatigue Test on 0.90 Per Cent Carbon Steel Wire.

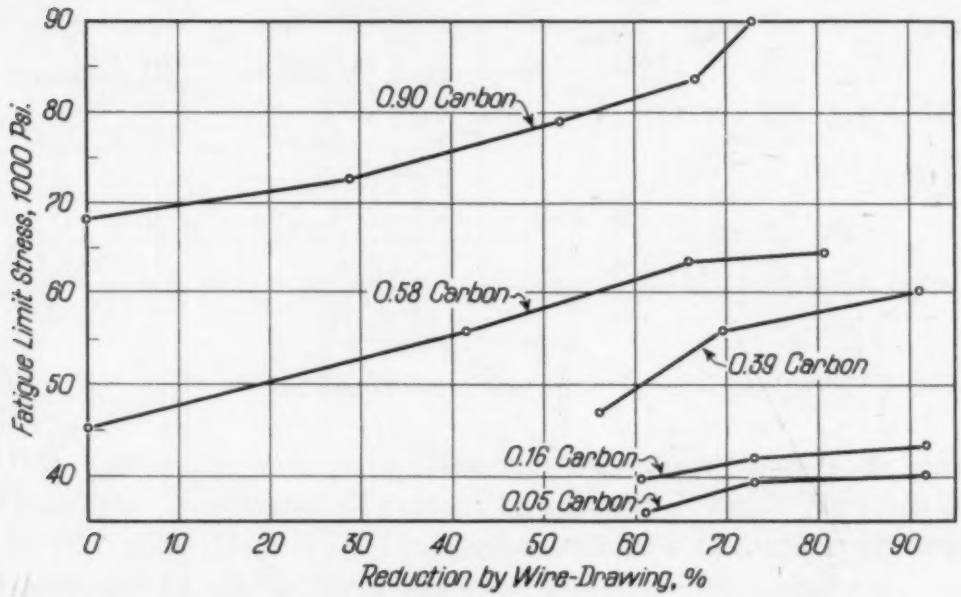

Fig. 14—Effect of Wire Drawing on Fatigue Limit Stress of Steel Wire.

reduction. The dashed line represents material drawn over 80 per cent reduction. It should be noted that the ratio between the fatigue limit and the tensile strength for the 0.90 per cent carbon wire is about the same value as for the 0.58 per cent carbon material. The reason for the lowering of the fatigue limit ratio with an increase in carbon content is one of conjecture. H. J. Gough (6) states that the fatigue limit can be correlated only to the ultimate tensile strength and that no adequate reason can, at present, be considered to account

satisfactorily for the correlation observed and should be regarded only as affording a useful empirical and approximate rule.

The lowering of the fatigue limit ratio with an increase in carbon content may be due to surface conditions or to the inherent properties

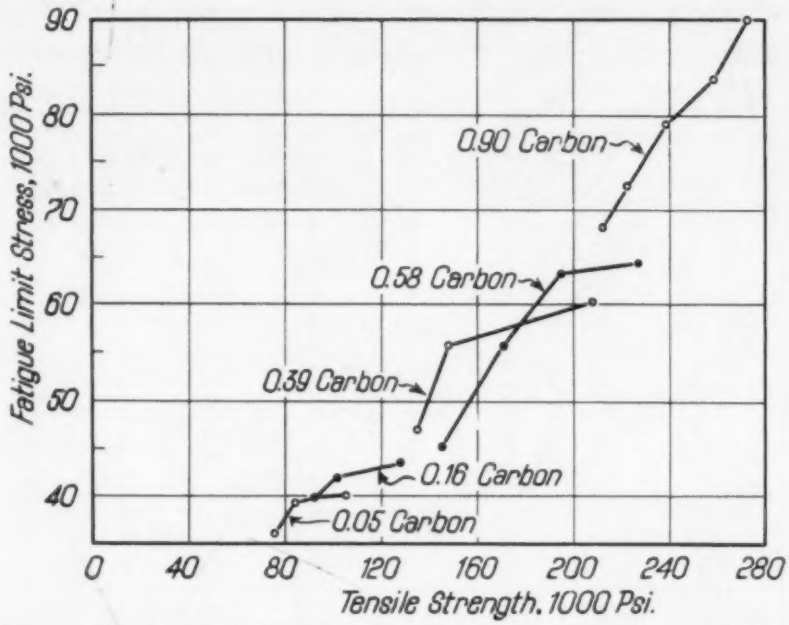

Fig. 15—Relation Between Fatigue and Tensile Strength of Steel Wire.

of the material. It is also noted that these materials of various carbon content showed a considerable drop in the fatigue ratio when cold-worked over 80 per cent reduction by wire drawing. These results are also included in Fig. 16, along with the amount of cold work. Gill and Goodacre (7) found in both decarburized wire and wire free from decarburization that the fatigue ratio was lowered when cold working was excessive. The 0.90 per cent carbon wire did not show any lowering of the fatigue ratio since it was only drawn to 72.6 per cent reduction.

Fatigue tests were also made on wires of five different carbon contents polished to 000 emery and the results are shown in Table I. In every case the fatigue properties were improved by the polishing. However, the decrease in the fatigue ratio with an increase in the carbon content is still evident in the polished wires.

The hardness of the material cannot be related directly to the fatigue properties since the fatigue ratio remains practically constant for the 0.90 per cent carbon wire from the patented condition up to 72.6 per cent reduction. From this phenomenon it is apparent that

the fatigue properties are dependent on some inherent characteristic other than hardness.

The physical properties of the decarburized wire were determined from hand-straightened specimens and are presented in Table II. The fatigue ratio of the bare wire averaged about 24 per cent which is considerably under the fatigue ratio of approximately 33 per

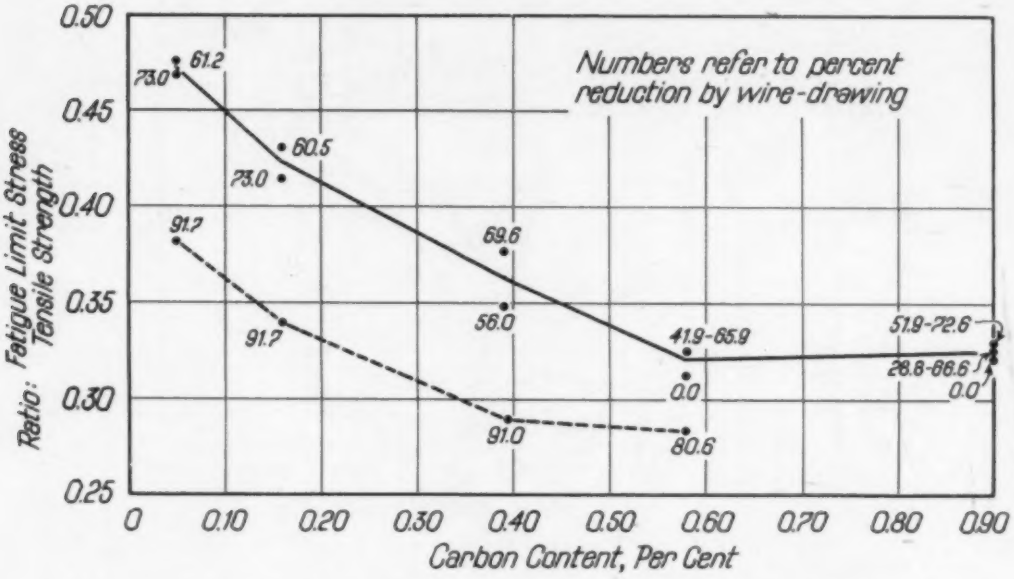

Fig. 16—Relation Between Fatigue Ratio and Carbon Content of Steel Wire.

cent for the 0.90 carbon and 0.58 carbon wire free from decarburization. The electro-galvanized material which had the same chemical composition as the bare wire had an average fatigue ratio of approximately 24 per cent which is the same value as that of the decarburized bare wire. The reason for this low fatigue limit is naturally explained by the decarburized surface of this material. Since the material at the surface is practically free from carbon, the fatigue limit is lowered to the extent of that of a low carbon steel. Once the fatigue crack starts in this material, it will progress throughout the higher carbon core since at the base of the fatigue crack the stresses are extremely high. The electro-galvanized wire had the same average fatigue ratio as the bare wire, indicating that the fatigue properties of this material are not affected by the electro-galvanized coating.

For general interest we have included the results of fatigue tests on cold drawn hot-galvanized bridge wire. The fatigue limit stress for this material was found to be 48,000 pounds per square inch, which corresponds to a fatigue ratio of 20.4 per cent, based on

the net diameter of the wire. Based on the gross diameter, the ratio would be 1 per cent higher. The extremely low fatigue ratio is probably due to both the effect of decarburization and the hot-galvanized coating.

The bending fatigue limit of heat treated galvanized bridge wire was found to be 50,000 pounds per square inch by Shelton and Swanger (8) or a fatigue ratio of 22 per cent. The fact that the fatigue stresses in suspension bridge cables are relatively low, probably account for the fact that cold drawn hot-galvanized bridge wire

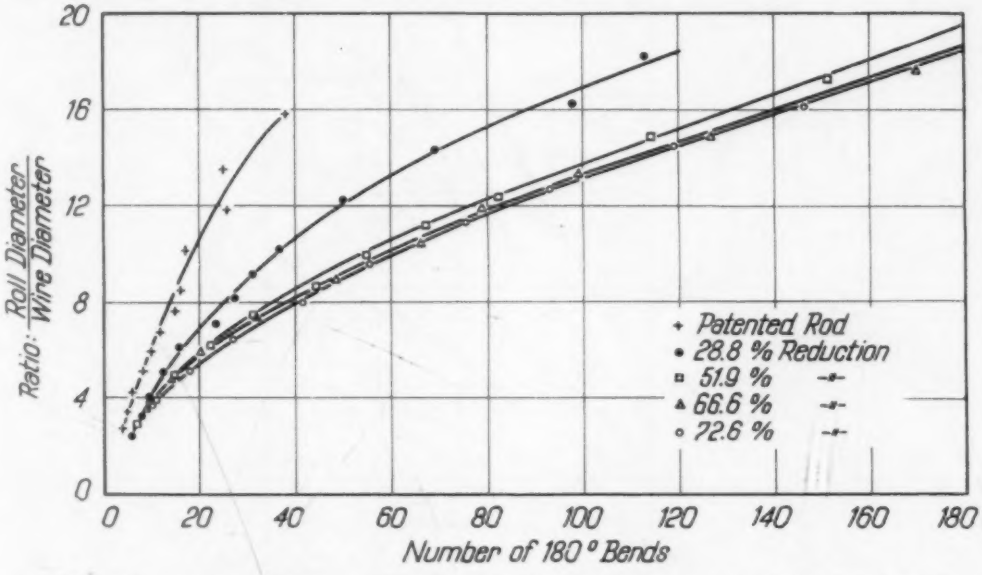

Fig. 17—Relation Between Roll Wire Ratio and Number of Bends for 0.90 Per Cent Carbon Wire.

has proved to be a satisfactory material for this purpose. However, the fatigue properties of wire in the main cables of suspension bridges should be maintained at the highest possible level.

Bending Properties—The wire bend test as carried out in this investigation was designed to study the effect of wire drawing on the bending properties of steel wire. The number of 180-degree bends that a wire can withstand before fracturing is used as the criterion for the relative bending properties. The severity of the bend test, as measured by the ratio of the roll diameter to the wire diameter, was also investigated. The ratio will hereinafter be termed the roll ratio.

The bend tests were made on the material included in Table I. This material was straightened by hand before testing. The results of the bend tests on the 0.90 per cent carbon wire are presented in

Fig. 17. The number of bends was found to be dependent upon the roll ratio and the amount of wire drawing. In the higher values of the roll ratio, the number of bends increased in proportion to the severity of the bend test. In this upper range a slight increase in the roll ratio will result in a relatively large increase in the number of bends. As the roll ratio approaches zero the bend curves con-

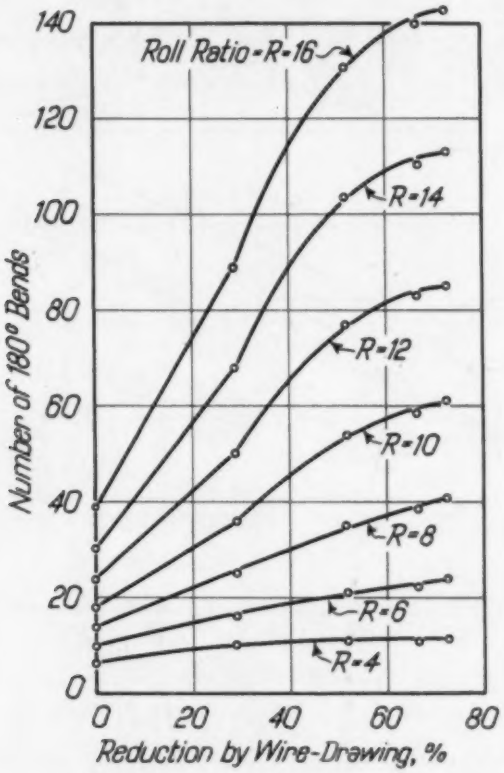

Fig. 18—Effect of Wire Drawing on the Bending Properties of 0.90 Per Cent Carbon Wire.

verge and in this range it is not possible to differentiate between the bending properties of wire cold drawn to different amounts.

For the patented wire the number of bends for a given roll ratio was found to increase with wire drawing. This relationship is illustrated in Fig. 18 where the bend test results of the 0.90 per cent carbon wire are presented for a number of roll ratios. The 0.90 per cent carbon wire was cold drawn 72.6 per cent reduction and up to this amount of wire drawing the bending properties were improved.

Fig. 18 clearly indicates the effect of the severity of the bend test on the test results. For a roll ratio of 4 there is little difference in the number of 180-degree bends for the 0.90 per cent carbon wire

drawn from zero to 72.6 per cent reduction. As the severity of the bend test is lessened by increasing the roll ratio a large difference in the bending properties of the wire is observed. It should be expected that the bending properties of wire should change with the amount of cold working by wire drawing. The flexibility of this bend test apparatus makes it possible to explore the bending properties of wire very much more completely than can be done by the conventional bend test apparatus.

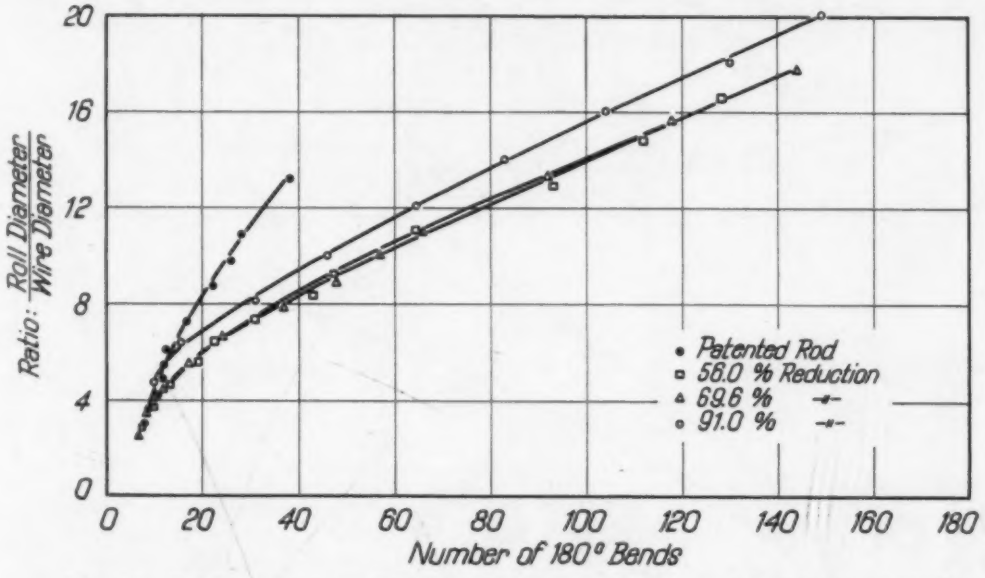

Fig. 19—Relation Between Roll Wire Ratio and Number of Bends for 0.39 Per Cent Carbon Wire.

The bending properties of the 0.39 per cent carbon wire are presented in Fig. 19. These curves have the same characteristics as those of the 0.90 per cent carbon wire except that when the material was severely cold drawn the number of bends, for a given roll ratio, decreased. The bending properties improved up to 69.6 per cent reduction but on further cold working to 91.0 per cent reduction the number of bends decreased. The effect of wire drawing on the 0.39 per cent carbon wire is illustrated in Fig. 20 and indicates that severe cold working by wire drawing injures the bending properties of wire. It also clearly demonstrates that the larger roll ratios are necessary to differentiate between the true bending properties of wire drawn to various percentages of reduction. Similar bend test results were obtained on the 0.58 carbon wire.

The results of the bend tests on the wire drawn from the hot rolled 0.16 carbon rod are presented in Fig. 21. There were only a

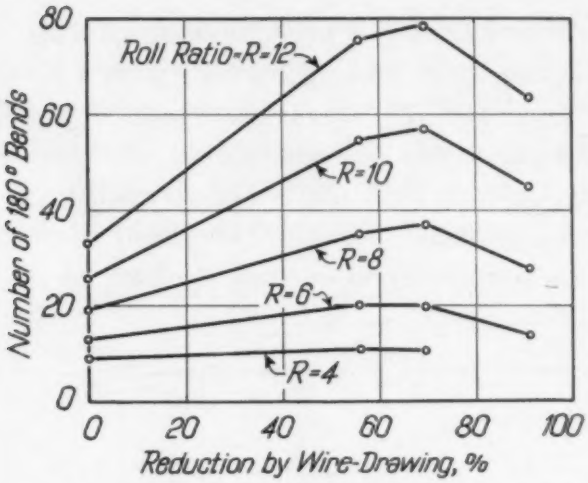

Fig. 20—Effect of Wire Drawing on the Bending Properties of 0.39 Per Cent Carbon Wire.

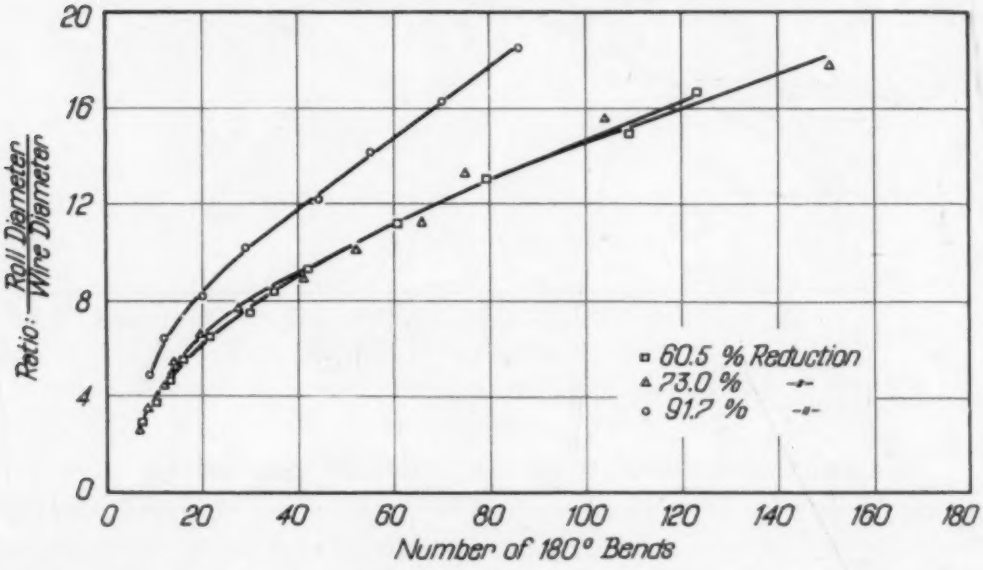

Fig. 21—Relation Between Roll Wire Ratio and Number of Bends for 0.16 Per Cent Carbon Wire.

few bend tests made on the hot-rolled rods since it was not possible to make a satisfactory test on this material. Bonzel (9) states that in patented wire the number of bends increases after the first few drafts and in the case of mild steel the number of bends decreases with wire drawing. The few bend tests made on the hot-rolled rods seem to confirm this statement. The bend test curves as presented in Fig. 21 have the same characteristic shape as those of the patented steel wire although none of the material tested was cold drawn less than 60 per cent reduction. This material shows a sharp decrease in the number of bends when cold drawn to 91.7 per cent reduction.

Fig. 22 shows the effect of wire drawing on the bending properties of the various materials tested. All of the bend curves with the exception of the 0.90 per cent carbon wire shows a distinct loss in

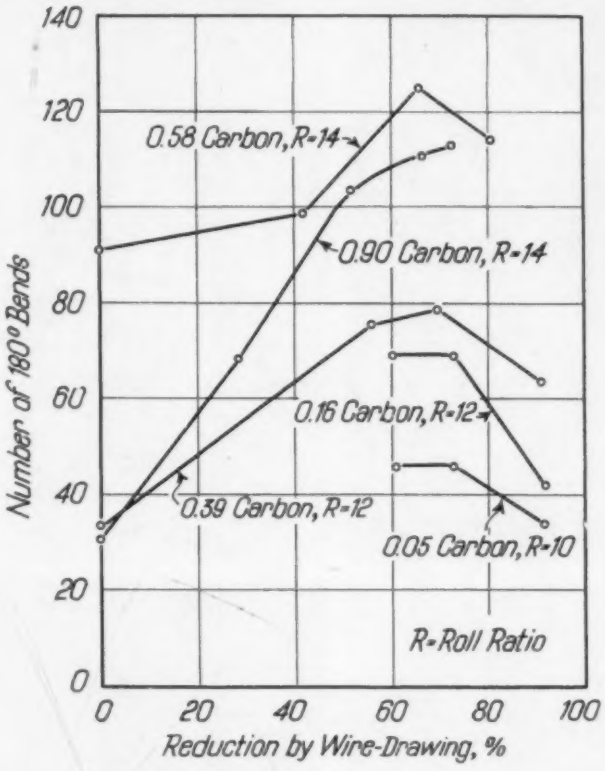

Fig. 22—Effect of Wire Drawing on the Bending Properties of Steel Wire.

the bending properties after severe cold drawing. The 0.90 per cent carbon wire was wire drawn 72.6 per cent, the 0.58 per cent carbon wire 80.6 per cent and all the other material over 0.90 per cent reduction. These tests show that the bending test can be used to differentiate between the true bending properties of wire, if the severity of the bend test is properly controlled.

General Discussion of Test Results

In this investigation the fatigue and bending properties of steel wire have been studied. The test results show that both the fatigue and bend tests as carried out in this investigation, can be used to study the effect of cold working on the physical properties of wire. The fatigue properties were found to increase in proportion to the tensile strength of the wire up to a critical amount of wire drawing,

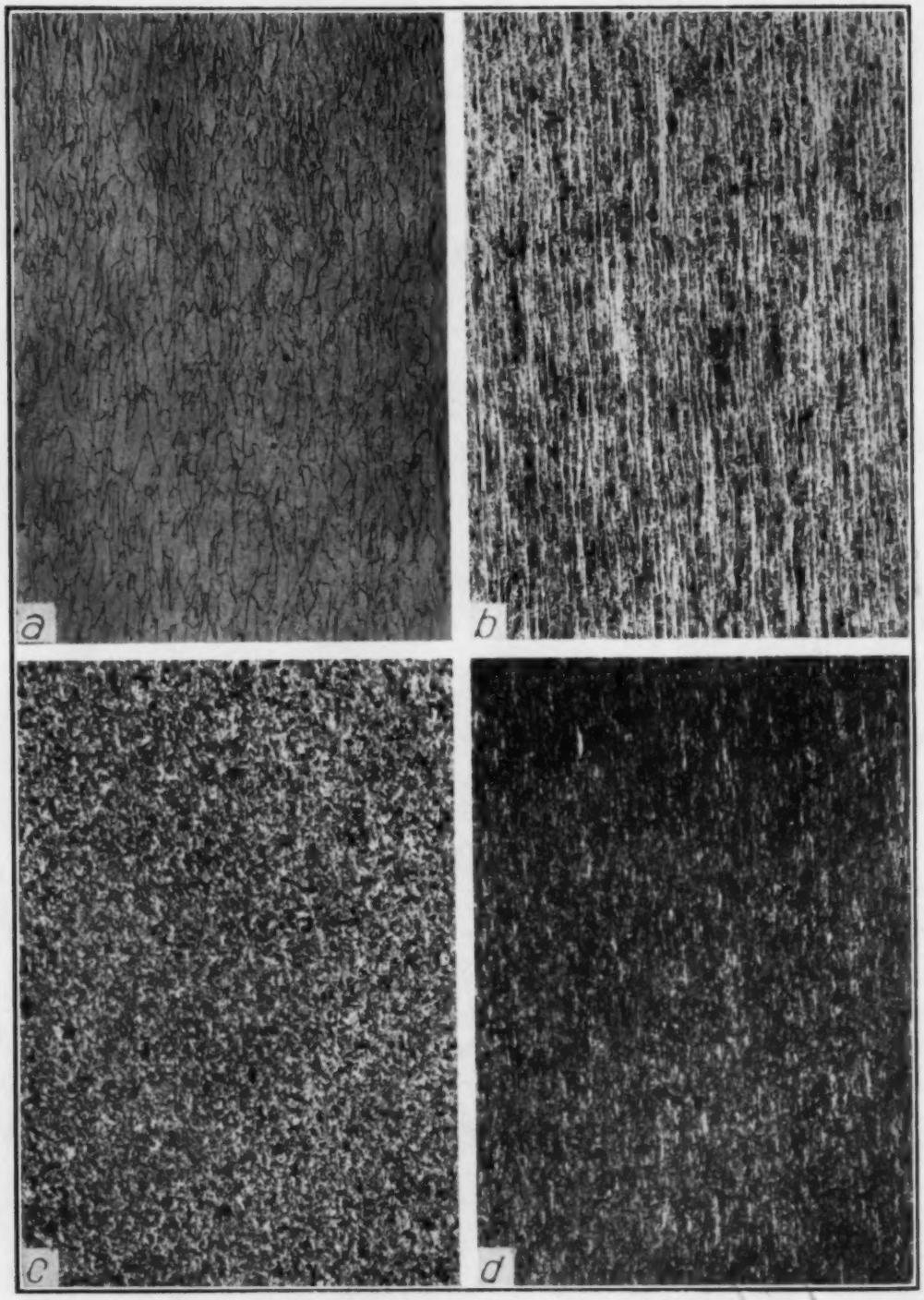

Fig. 23—Photomicrograph of Cold-Drawn 0.05 Carbon and 0.58 Carbon Steel Wire. × 100. a.—0.05 Per Cent Carbon. 61.2 Per Cent Reduction. b.—0.05 Per Cent Carbon. 91.7 Per Cent Reduction. c.—0.58 Per Cent Carbon. 41.9 Per Cent Reduction. d.—0.58 Per Cent Carbon. 80.6 Per Cent Reduction.

at which point both the fatigue and bending properties show a decided change.

A metallographic study of the cold drawn wire was made on the 0.05 and 0.58 per cent carbon wire and the photomicrographs are shown in Fig. 23. These illustrate the effect of cold drawing on the structure of steel wire. The extreme amount of fibering is clearly shown in the 0.05 per cent carbon wire drawn 91.7 per cent reduction. However, this metallographic examination does not indicate any decided change in the physical properties of the wire.

To investigate the problem more extensively, an examination of the internal structure of the wire was made with X-rays. By means of X-rays any change in the orientation of the grains in a polycrystalline material by wire drawing or other means of cold working can be identified. When a polycrystalline material is cold-worked the individual grains, which formerly were oriented at random, tend to orient themselves in a particular manner. In the case of wire drawing the deformation is always in the same manner so that the grains tend to orient in the same direction. As a result, the structure of the metal has a preferred orientation and the material can no longer be considered to be isotropic. The properties of wire in the longitudinal direction will thus be different from the properties in the transverse direction.

A monochromatic X-ray photograph made by reflecting the X-rays from the surface of the polycrystalline material will show a number of concentric rings of uniform density if the crystals are oriented at random. This is due to the reflection of the X-rays from the principal planes of the crystals. However, if the crystals are oriented so that a particular crystallographic direction lies in the axis of the wire, the material will no longer be isotropic and the Debye-Scherrer rings are broken up into patches corresponding to the preferred positions of the crystallites. The intensity of these patches is dependent upon the degree of preferred orientation.

Elam (10) reports that as a result of wire drawing the direction taken up by the crystals of a body-centered cubic lattice is such that the face diagonal of the cube, i.e., [110], lies parallel to the wire axis and that preferred orientation was more complete in the inside layers of a wire.

The X-ray photographs of the 0.05 per cent carbon wire drawn 73 per cent is shown in Fig. 24. Both the surface and the core of the wire were investigated. In order to reflect the X-rays from the core of the wire the outside of the wire was dissolved with acid. Both the surface and the core of this material show by the varying

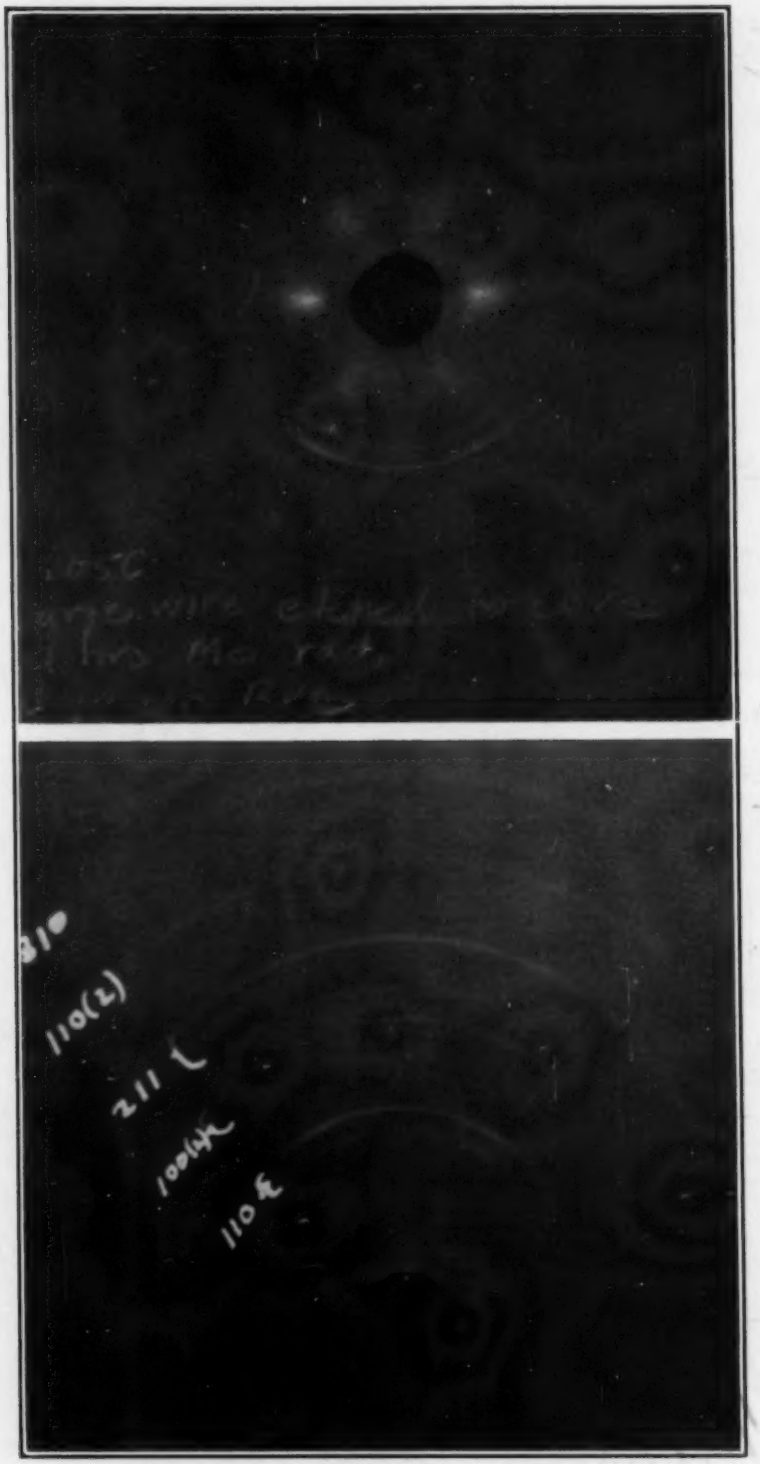

Fig. 24—X-Ray Diffraction Patterns of 0.05 Per Cent Carbon Wire Cold Drawn 73.0 Per Cent Reduction. Top—Core. Lower —Surface.

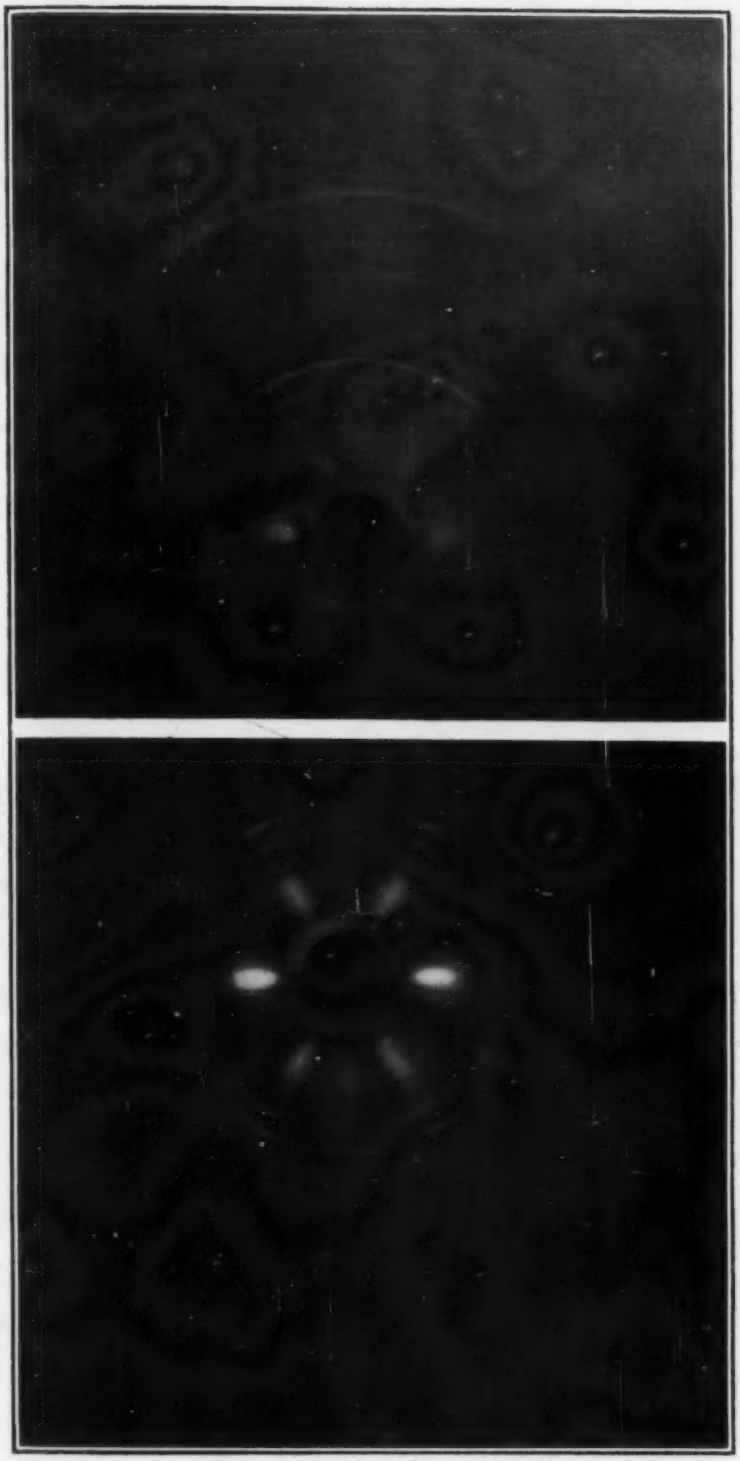

Fig. 25—X-Ray Diffraction Patterns of 0.05 Per Cent Carbon Wire Cold Drawn 91.7 Per Cent Reduction. Top—Surface. Lower—Core.

intensity of the rings that there is some indication of preferred orientation. The X-ray photographs of the 0.05 per cent carbon wire drawn 91.7 per cent reduction are shown in Fig. 25. The surface of this highly drawn material indicates some preferred orientation but the core of the wire indicates considerable preferred orientation.

A similar investigation of the 0.58 per cent carbon wire was made by means of X-rays. The results of the examination of the surface and core of the 0.58 per cent carbon material drawn 41.9 per cent reduction indicated a slight amount of preferred orientation. The reflection photographs of the 0.58 per cent carbon wire drawn 80.6 per cent reduction are shown in Fig. 26. The surface of the material indicates some preferred orientation while the core of the wire exhibits somewhat more preferred orientation than the surface.

Elam (11) reports that various investigators have found that the core of wires have the most perfect fiber-structure and that the tensile strength of the core was higher than that of the outer layers of hard drawn wire.

In extremely cold drawn wire we therefore have a condition in which the orientation of the wire is variable over the cross section. If the tensile strength of the core of highly drawn wire is greater than the outer layers the reason for the lowering of the fatigue ratio may be explained. The tensile strength is the average strength of the material over the entire cross section of the wire. The bending fatigue limit stress is largely influenced by the characteristics of the material at the surface of the wire since the maximum bending stresses occur at the surface. If the surface of the wire is not as strong as the core a drop in the fatigue ratio is therefore to be expected. This condition is similar to that in which the surface of the wire is decarburized.

A drop in the fatigue ratio does not necessarily mean that the wire has been actually damaged by wire drawing as far as fatigue is concerned, since no internal cracks or fissures were visible. As shown in Fig. 14 the fatigue limit stress increases with wire drawing up to 90 per cent reduction which is as far as this study has investigated. However, in the latter stages of cold working the fatigue limit stress does not increase in proportion to the tensile strength.

The bend test results as shown in Fig. 22 indicate that when wire has been severely cold drawn it is not able to withstand highly localized stresses which cause plastic deformation as well as wire

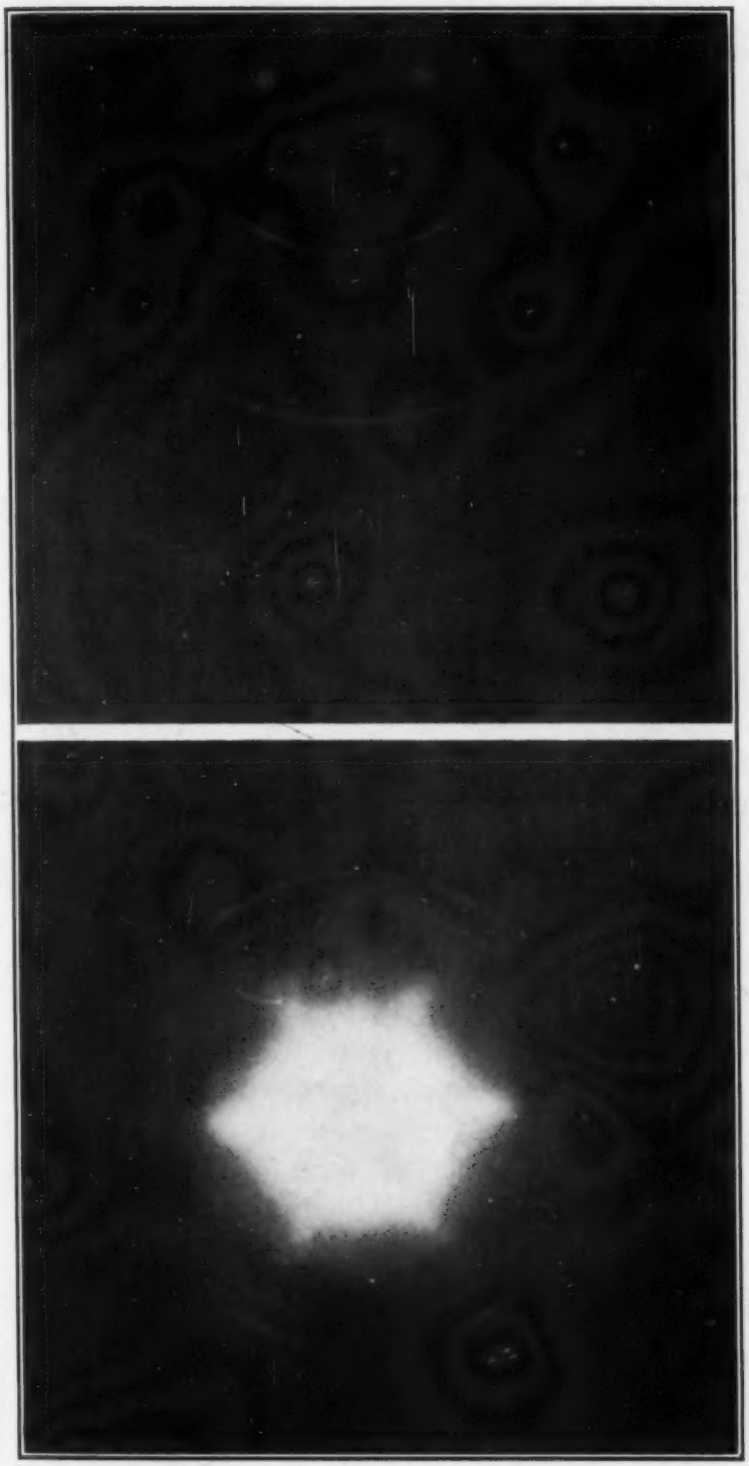

Fig. 26—X-Ray Diffraction Patterns of 0.58 Per Cent Carbon Wire Cold Drawn 80.6 Per Cent Reduction. Top—Surface. Lower—Core.

drawn to an intermediate amount of cold drawing. It is for this reason that the bend test as carried out in this investigation, might be used as an index to determine the amount of cold drawing most advisable for a given service. Wire should not be cold drawn to a maximum and then be expected to undergo plastic deformation in service without danger of an early breakdown. However, all features of a given problem should be given consideration because relatively heavy reductions might be most desirable in order to provide physical characteristics essential to satisfactory performance under special service conditions.

The work on the fatigue properties of steel wire is being continued at the Fritz Engineering Laboratory. The next investigation will include a study on the effect of the rate of drafting on the properties of steel wire.

Conclusions

1. The characteristics of the fatigue test results on steel wire are influenced by the carbon content of the material. The fatigue limit of a low carbon material should be determined by a fatigue test of at least 10,000,000 cycles in duration. For higher carbon materials, the length of the test may be considerably less.

2. Normal cold working by means of wire drawing increases the fatigue limit of steel wire in proportion to the tensile strength of the wire. However, after the cold working exceeds a critical amount, the ratio between the fatigue limit and the tensile strength decreases.

3. The ratio between the fatigue limit and the tensile strength decreases with an increase in carbon content, for materials free from decarburization.

4. Improving the surface of wire by polishing, increases the fatigue properties of wire.

5. Decarburization on the surface of cold drawn wire reduces the fatigue properties of wire. The depth of decarburization does not seem to have any effect on the fatigue ratio.

6. An electro-galvanized coating does not lower the fatigue ratio of a decarburized wire.

7. The bending fatigue properties of cold drawn hot-galvanized bridge wire may be approximately the same as a heat treated hot-galvanized bridge wire.

8. The bending properties of patented steel wire increase with

cold work up to a critical amount. Beyond this point the bending properties decrease.

9. The true bending properties of steel wire may be determined by controlling the severity of the bend test.

10. Both the bending fatigue test and bend test may be included in the several factors which should be considered in deciding upon the desired amount of cold drawing.

11. The effect of wire drawing on the internal structure of metallic crystals as shown by X-ray photographs is such that the individual crystals tend to orient themselves into one position. The amount of orientation is more apparent when cold working is excessive. The maximum amount of orientation takes place in the core of the wire.

Acknowledgment

The author wishes to express his appreciation to C. W. Meyers of the American Steel and Wire Company and to L. H. Winkler of the Bethlehem Steel Company for the material used in this investigation and for their suggestions and advice; to J. N. Kenyon of Columbia University for checking the accuracy of the wire fatigue machine used in this study and to B. K. Daubenspeck, Research Fellow in Chemistry at Lehigh University for the X-ray photographs included in this paper. To the Fritz Engineering Laboratory Staff which includes Professor Hale Sutherland, Director and Professor Bruce Johnston, Assistant Director, we express our sincere thanks for the co-operation received in carrying out this investigation. To Professor Inge Lyse, formerly in charge of the Fritz Engineering Laboratory and now at the Norges Tekniske Hoiskole, we express our sincere appreciation for making this investigation possible.

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DISCUSSION

Written Discussion: By C. W. Meyers, assistant manager, Metallurgical Dept., American Steel & Wire Co., Cleveland.

The information incorporated in this well-prepared paper by Mr. Godfrey is of special interest to us because of the fact that we are making fatigue tests on similar equipment and also on equipment designed to test stranded wires of various types. In the main, our findings have been in accord with those of Mr. Godfrey. Certain questions arise, however, bearing on coated wires which may be of interest to those concerned with fatigue studies.

Coatings on wire (particularly when stranded) appear, from our tests, to impart to the wire certain of the fatigue properties of the coating material. In strands, or rope, the coefficient of friction of the coating material functions to increase or decrease the friction between the moving components during the fatigue test and thereby intensify or relieve somewhat the actual effect of fatigue. The actual fatigue characteristics of the coating material also affect the fatigue value of the wire. It has been found, as indicated later, that a wire with a fairly low fatigue value coating, such as copper, fails at a notably lower fatigue ratio than zinc coated wire, reflecting the relatively better fatigue value of the latter material. Contrary to general opinion, our tests appear to indicate that a fatigue crack, starting on the surface of the wire propagates itself through the coating into the base metal with no diminution in rate. This may be accounted for by the fact that the notch effect, with attendant stress concentrations, starts failure in the base metal at once.

Low carbon hot galvanized steel wire of 89,000 pounds per square inch tensile strength has a fatigue ratio of 42 per cent, while hot galvanized steel bridge wire of 213,000 pounds per square inch tensile value has a fatigue ratio of 27 per cent. A copper coated wire, on the other hand, having a tensile strength of 134,000 pounds per square inch, has a fatigue ratio of only 17 per cent.

Material	Tensile Strength Lbs. Per Sq. In.	Fatigue Strength Lbs. Per Sq. In.	Ratio Per Cent
Copper coated wire	134,000	23,000	17
Hot galvanized steel	89,000	38,000	42
Hot galvanized steel	213,000	57,500	27

To analyze the more specific figures as outlined above it will be noted that galvanizing has a marked effect in reducing the fatigue ratio of the higher tensile wire and a minor effect in the case of the lower tensile steel.

Here, as well as in the galvanized wire figures given in Mr. Godfrey's paper, two factors may be responsible for these results.

First, the differential between the strengths of the steel and the coating material being less in the case of the low tensile wire will tend to make the reduced fatigue limit less effective. Second, the high stress concentration from the notch effect of the initial fatigue crack in the outer fibers will be less severe in the lower tensile material. It may be noted here that this second factor may also play a part in the characteristic noticed by Mr. Godfrey that in fatigue tests of high carbon steel fewer cycles are required to determine the fatigue limit.

We may again refer to copper to more definitely illustrate this point. Copper, regardless of its being higher in tensile strength than zinc, produces a greater reduction in the fatigue strength of the high tensile core. (In the case of the strand, mentioned before, a reasonable explanation has been given for the earlier failure of copper coated wires.) In the case of a single wire the problem may be approached from another viewpoint. It is quite possible that this relatively high strength coating with its sharp line of demarcation between coating and high strength steel base causes more severe stress concentration than the weaker zinc coating with its more gradual strength gradient between the soft zinc, the zinc iron alloy beneath, and the steel wire.

The case for the bend test is amply covered by Mr. Godfrey. It might be interesting to point out, in this connection, that the bend test is still extensively used in the industry. Proper apparatus, as discussed in the paper, can undoubtedly go a long way toward increasing the efficiency of the test. Wire bending machines as used in the industry are considerably less intricate and accurate than equipment used by the author in preparing this paper. In order to adapt the recommended bend test machine to the multitudinous sizes of wire manufactured in the average wire mill, it would, of course, be necessary to provide a great number of rolls and fixtures. The time element in changing from one to the other would also be a considerable factor. Notwithstanding these difficulties in changing from the "rough and ready" practice of today, it might pay industry well to adopt the more refined method. For comparison, however, it would be interesting to see sets of values of similar steels tested by both methods tabulated in detail.

Mr. Godfrey has exhibited a commendable grasp of the problem and the difficulties besetting such an investigation and is to be complimented on the scope of his approach to such an involved subject.

Written Discussion: By Wilber E. Harvey, assistant chief metallurgist, John A. Roeblings Sons Co., Trenton, N. J.

Mr. Godfrey's paper is particularly interesting because supplementary metallographic and X-ray evidence is offered for consideration in addition to a complete series of physical tests. Too frequently it is impossible for an author to present as complete a picture of a material under investigation as Mr. Godfrey has done in this investigation.

The very nature of the contents of the paper makes a discussion difficult. A great amount of physical testing data is present and is welcomed by the student of the wire industry. The results obtained seem perfectly sound.

The author's interpretation of the cause or mechanism for the lowering of fatigue-tensile ratio and for the lowering of the bend properties of severely drawn wire attracts attention. Even a discussion of this phase may lead the discusser in channels of conjecture which may be refuted or substantiated by present available evidence. Too little is known regarding the analysis of stresses imposed during the passage of a rod or wire through a die. The problem contains many variables such as die angle, per cent reduction of wire drawing, etc.

Quoting Mr. Godfrey, page 160, paragraph 2:

"Elam (11) reports that various investigators have found that the core of wires have the most perfect fiber-structure and that the tensile strength of the core was higher than that of the outer layers of hard drawn wire."

There appears to be little doubt that the degree of preferred orientation in a hard drawn wire does increase in progressing from the surface layers to the center of the wire which is in agreement with the statement that the most perfect fiber-structure may exist in the core of the wire. However, it would seem that an extended discussion of the higher tensile strength prevailing in the core with respect to the surface layers would have been desirable.

In general, the residual stresses in the surface layers of a drawn wire are tensile while the residual stresses in the core of a drawn wire are compressive. Let us assume a wire with a tensile strength of 200,000 pounds per square inch. If the residual tensile stress in the surface layers is X pounds per square inch then the net or effective tensile strength of the surface layers is 200,000 − X pounds per square inch. If the residual compressive stress in the core of the wire is Y pounds per square inch then the net or effective tensile strength of the core is 200,000 + Y pounds per square inch. Thus as a combined cross section the core may be considered as being able to resist higher applied loads in tension.

If it were possible to test the core of the wire removed from the wire so that the effects of trapped stresses were largely absent, would the core possess a higher tensile strength than the surface layers?

In other words, does the author believe the higher tensile strength of the core to be inherent and due to a greater amount of work-hardening or is the higher strength of the core simply due to trapped stresses?

A study of the micrographs leads to the question as to whether the caption under Fig. 23 (b) is correct. The microstructure as illustrated appears to be that of a higher carbon steel than 0.05 per cent. However, it is possible that the reproduction of the original prints may be misleading.

Written Discussion: By G. W. Stickley, Aluminum Research Laboratories, New Kensington, Pa.

The core of steel-reenforced aluminum cable as used in many high voltage transmission lines and rural distribution lines employs hot-dip galvanized cold drawn steel wire of practically the same composition as the wire used in the tests summarized in Table II of this paper. Using Haigh-Robertson fatigue machines, in which the principle is the same as in the fatigue machines described in the paper, endurance limits of 54,000 to 71,000 pounds per square inch have been obtained for various wire diameters from 0.188 in. to 0.083 in. respectively. The average ratio of endurance limit to tensile strength is about

0.25. The stresses are based on the net diameters of the steel wires after deducting the thickness of the galvanizing.

Because it is important that the specimens used in the fatigue tests be perfectly straight, the wire was machine-straightened, this operation being performed with the machine adjusted so that the amount of working was at a minimum consistent with satisfactory straightening. Contrary to the statement made by the author in his paper, we found that this straightening operation had a definitely harmful effect upon some of the tensile properties. Although the average decrease in tensile strength was less than 1 per cent, the yield strength was decreased about 7 per cent and the decrease in elongation (in 10 inches) was almost 10 per cent.

Author's Reply

The author is very appreciative of the discussion presented. The comments and test results contributed by Mr. Meyers form a valuable supplement to this paper. In regard to the effect of copper and zinc coatings on the fatigue properties of a single wire, Mr. Meyers attributes the lower fatigue ratio of the copper coated wire to the possibility of a more severe stress concentration due to the sharp line of demarcation between the coating and the high strength steel. Another explanation of this relatively low fatigue ratio might be explained from a different viewpoint. In computing the bending stresses in a specimen we assume that the stress is zero at the neutral axis and increases in direct proportion to the distance from the neutral axis. This is only true, however, when the modulus of elasticity is the same for the entire cross section of the wire. In the case of a coated wire, the actual stress in the coating, for a given amount of bending, is dependent upon the modulus of elasticity of the material. Since the physical properties of the zinc and copper coatings are very different, the actual stress in the coatings for the same amount of strain would not be the same. The effect of the two types of coatings is therefore dependent upon their individual fatigue properties and the actual stress in the coatings. As Mr. Meyers has stated, the fatigue crack starts on the surface of the wire and propagates itself through the coating into the base metal. It should be emphasized that for a given amount of bending the true stress in the coating is dependent upon its modulus of elasticity.

Mr. Harvey has discussed an important problem in connection with the fatigue characteristics of steel wire and raises the question as to the reason for the apparent greater strength of the core of an extremely cold-drawn wire in relation to the surface layers. The author believes that the residual stresses would have little effect on the tensile strength of the core or surface layers since at the ultimate load the amount of plastic deformation is so great that the effect of the residual elastic strains would be eliminated. It would seem that the residual stresses in cold-drawn wire might have some effect on the fatigue strength, since, as Mr. Harvey states, the residual stresses in the surface layers are tensile. The test results show, however, that the residual stresses do not have any apparent effect on the fatigue strength. For example, the 0.90 per cent carbon wire has approximately the same fatigue ratio for the various sizes ranging from zero to 72.6 per cent reduction.

The apparent higher strength of the core is believed to be due to the greater amount of preferred orientation at the core. This does not necessarily mean that the core has been subjected to a greater amount of cold working than the surface layers but that the cold working was probably more uniform. The author agrees with Mr. Harvey that the problem contains many variables such as the rate of drafting, the die angle, etc., and it is our purpose to investigate some of these problems more fully in the future.

Fig. 23b, referred to by Mr. Harvey, has been checked and although the reproduction appears to be of a higher carbon content, the material in question was found to be a 0.05 per cent carbon steel.

Mr. Stickley reports that the machine straightening operation used for the straightening of the wire fatigue specimens has a definitely harmful effect upon some of the tensile properties. These properties include the tensile strength, yield strength and the elongation. We have also found that the tensile and yield strengths have been reduced by the straightening operation but we have not found that the ductility of the material has been lowered. In our present study on the effect of the rate of drafting on the physical properties of cold-drawn steel wire we have consistently found that the ductility as measured by the elongation and reduction of area has actually been improved by the machine straightening operation.

We are continuing our present investigation on the effect of the rate of drafting on the physical properties of steel wire. This study includes rates of drafting ranging from 10 to 40 per cent on 0.70 and 0.25 per cent carbon steel wire.

FACTORS AFFECTING THE ACTIVITY OF CARBURIZING COMPOUNDS

By Mack Sutton and R. A. Ragatz

Abstract

Quantitative data are presented on the energizing action of barium, calcium and sodium carbonates with hardwood charcoal. The variables investigated were temperature and per cent energizer. Data are given on the relative effectiveness of various carbonaceous substances when energized with barium, calcium, or sodium carbonate. The changes that occur in carburizing compounds when used were studied and results are presented; and finally data on the regeneration of various carburizing compounds on aging after use.

Introduction

THE work described in this paper was performed with the object of filling in some of the gaps in our existing knowledge of the behavior of compounds of the solid type, or, in some instances, of amplifying the scant data that are available. The present investigation was directed along the following lines: (a) The effect of energizer concentration and carburizing temperature when using hardwood charcoal as the solid carbonaceous substance, and when using the carbonates of barium, calcium and sodium as energizer materials. (b) The relative effectiveness of various types of carbonaceous substances when using barium, calcium and sodium carbonates as energizers. (c) The changes occuring in compounds of the solid type on use. (d) The capacity of energized compounds to regenerate on aging after use.

Experimental Procedures

Preparation of Carburizing Compounds—The solid carbonaceous materials were reduced to finely powdered form, as were the energizer chemicals. Just before use, they were mixed thoroughly in order to insure an even distribution of the energizer throughout

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the carburizing compound. This procedure would, it was believed, achieve more reproducible results in the experimental work than if a granular material were used which had the energizer attached to the surfaces of the granules. The latter procedure would have necessitated the use of a binding agent, and the presence of such materials, which usually are organic substances, would doubtless have affected the results to some extent and thus introduced an added complication in the interpretation of the experimental data.

Some objection may, perhaps, be raised against the use of a carburizing compound in finely divided form. While many statements may be cited from the literature which assert that finely divided materials will not carburize properly, it has nevertheless been the writers' invariable experience that if the factor of energizer segregation does not enter, a finely divided compound will carburize more rapidly than a coarser compound, both having the same concentration of energizer. This experience verifies the statement made by Rodman (1)[1] that "finer sizes of uniformly mixed carburizer will carburize more rapidly than coarser sizes, once they have been heated thoroughly. The trouble with these finer sizes is low thermal conductivity". Suffice to say, that the finely divided mixtures of carbonaceous substance and energizer material used in the present experimental work showed an excellent degree of reproducibility, and also a high order of activity when an effective energizer was used in proper amount.

In most of the experimental work, no particular effort was made to dry the carbonaceous substances before use. It was, however, the usual practice to make an occasional moisture determination of the carbonaceous materials, and to take account of the moisture in proportioning the mixtures. Merely as a matter of convenience, the energizer chemicals were dried and stored in desiccators. It may be pointed out that statements have frequently been made to the effect that moisture in a carburizing compound will exert an adverse effect on its activity. Such statements, however, are usually expressions of opinion, rather than conclusions drawn from experimental data. In the recent carburizing symposium held before this society, Lewis (2) states, "it is hard to conceive that small amounts of water heated to some 1700 degrees Fahr. in the presence of carbon can remain as steam and do harm to the work . . . . The writer has never been able to definitely trace soft spots to this source,

[1]The figures appearing in parentheses refer to the bibliography appended to this paper.

and it is his opinion that entirely too much weight is given to this subject of absorbed moisture in carburizing compounds." This statement is in accordance with the experience of the present writers, who have employed experimental mixes containing as high as 5 per cent moisture without obtaining any reduction in the carburizing activity of the compound. The carbonaceous substances used in this experimental work seldom contained over 3 per cent moisture, and no evidence was obtained to indicate that this small quantity had any adverse influence on the results.

Steel Specimens—Steel cylinders $\frac{7}{16}$ inch in diameter and 1 inch long were used throughout the work. Two lots of S.A.E. 1020 steel of the following analysis were used.

	SR 39 Per Cent	SR 40 Per Cent
Carbon	0.17	0.20
Manganese	0.49	0.47
Phosphorus	0.018	0.016
Sulphur	0.039	0.029

Both steels exhibited identical rates of carburization under the same conditions, and both exhibited normal cases after carburization. The steel was obtained in the form of ½ inch diameter hot-rolled rounds, and specimens were machined to the dimensions given above. They were finished with No. 0 emery cloth, and then stored in oil until needed. Before use they were washed thoroughly in gasoline, and finally, in alcohol, after which they were dried and weighed.

Carburizing Retorts—The retorts were made of standard 1¼ inch pipe, using 4-inch nipples, capped with black iron caps. In some of the earlier tests, wrought iron pipe was used, without making any effort to remove the scale normally present on the inner surface of the pipe. When it was discovered that sodium carbonate tended to react with the scale to some degree, the wrought iron pipe was replaced with galvanized steel pipe, which was pickled prior to use to obtain complete removal of the zinc coating. The inner surfaces of the caps were machined to expose a clean metal surface. Thus, in most of the work, the retorts presented clean, scale-free metal surfaces on the inside.

In performing a carburizing test, each retort held two of the standard specimens, located axially and surrounded with an adequate thickness of the carburizing compound.

Furnace and Temperature Control Equipment—Carburizing treatments were carried out in an electric furnace, with a muffle

7⅝ inches wide by 5⅜ inches high and 14 inches long. The muffle was of sufficient size to accept four of the standard retorts, which were bundled together, and so placed as to be in the region of uniform temperature in the muffle.

The furnace was equipped with a chromel-alumel couple, which was connected to a controller-recorder of the potentiometric type. The couple was calibrated at frequent intervals by comparison with a noble metal couple that had been calibrated by the National Bureau of Standards.

Standard Carburizing Cycle—The assembly of four retorts was inserted into the cold furnace and the maximum heating current was then turned on. The time was noted when the desired temperature was attained. The retorts were maintained at the desired temperature for 7 hours, after which they were removed and air-cooled.

Evaluation of Degree of Carburization—The degree of carburization was evaluated by determining the weight increase per unit area and also by measuring the case depth under the microscope. In measuring case depths, two values were determined, total case depth and the depth of the hypereutectoid plus eutectoid zones. The measurement of total case depth is somewhat uncertain as it is difficult to tell with a high degree of exactness the point where the carbon content drops to that of the uncarburized steel. The measurement of the hypereutectoid plus eutectoid region is, however, quite exact, for it is easy to locate the first particles of free ferrite in the case.

The results obtained by these methods were in excellent agreement, except in those instances where the weight increases were in error because of graphite deposition. Every figure for weight increase or of case depth given in this paper is the average for at least two specimens, and frequently more.

Effect of Temperature and Energizer Concentration

Shepherd (3) carried out tests on compounds containing 0, 2½, 5, 22½ and 40 per cent barium carbonate mixed with wood charcoal. He found that the compound with 2½ per cent barium carbonate was just as effective as the others with higher percentages. The boxes containing the specimens were heated to 1600 degrees Fahr. (870 degrees Cent.) in 8 hours, held for various lengths of

time and air-cooled. The effectiveness of the carburizing treatment was evaluated by machining successive layers from the cylindrical bars, analyzing them for carbon and finally plotting curves showing the relation between distance from the outer surface and per cent carbon in the steel.

Takahashi (4) investigated the effect of energizer concentration when using charcoal with the carbonates of barium, strontium, lithium, sodium and potassium. Degree of carburization was evaluated by plotting curves showing the relation between carbon content and distance from the outer surface. These curves were apparently based solely upon microscopic examination, hence are of doubtful accuracy.

Knowlton (5) worked with preheated charcoal, to which various amounts of energizer up to some 28 per cent were added. The energizer in all cases was a mixture of 3 parts sodium carbonate, 3 parts calcium carbonate and 9.75 parts barium carbonate. The carburizing test involved heating 6 hours at 1700 degrees Fahr. (925 degrees Cent.) and results were evaluated by measuring case depths under the microscope. The curves relating case depth versus per cent energizer indicate that increasing the energizer concentration beyond 4 per cent produces but little increase in rate of carburization.

Widrig (6) states that an increase in rate of carburization is obtained up to approximately 8 per cent energizer, beyond which there is but little increase in rate of carburization. He recommends that in commercial work sufficient fresh compound be added to the used compound to maintain the energizer concentration between 8 and 10 per cent.

In the present investigation, a hardwood charcoal from Tennessee was used as the carbonaceous base. This selection was made because of the widespread use of charcoal in commercial carburizing compounds. The specific material used is actually employed in large quantities by a prominent manufacturer of carburizing compounds. It was deemed desirable to investigate the effect of various additions of barium carbonate, calcium carbonate and sodium carbonate, because these three energizers are used in commercial compounds to practically the complete exclusion of other catalytic agents. Energizer concentrations up to 15 per cent, varied in appropriate steps, were employed. Temperatures in 50-degree intervals from 950 to 650 degrees Cent. (1740 to 1200 degrees Fahr.)

were employed. The other details of precedure were as indicated previously.

The experimental results are summarized in Figs. 1 to 20. Figs. 1 to 5 show the relation between weight increase and temperature, each figure being for a fixed percentage of energizer. Figs. 6 to 10 are similar to Figs. 1 to 5, but with case depths plotted against carburizing temperature. Figs. 11 to 15 show weight increase as a function of energizer concentration, each figure being for a fixed carburizing temperature. Figs. 16 to 20 are similar to Figs. 11 to 15, but show case depths versus energizer concentration.

In working with the specimens, some significant differences in surface appearance were noted. The samples carburized with plain charcoal without exception exhibited clean, light appearing surfaces which were but slightly different in appearance from the specimens prior to carburization. All samples carburized with $CaCO_3$ as the energizer had exactly the same appearance as those carburized in the unenergized charcoal. When $BaCO_3$ and Na_2CO_3 were used as energizers, however, it was observed that if the temperature were high enough and if sufficient energizer were present, a marked blackening of the surface occurred due to precipitation of graphite. For example, at 950 degrees Cent. (1742 degree Fahr.) when using Na_2CO_3 as energizer, a concentration as low at 1.25 per cent Na_2CO_3 induced visible deposition of graphite on the steel surfaces. As the concentration of Na_2CO_3 increased up to 10 per cent, progressively greater amounts of graphite were observed, while beyond 10 per cent there was no noticeable increase in quantity. At 950 degrees Cent. (1740 degrees Fahr.) with $BaCO_3$ as energizer, deposition of graphite was first noted at a concentration of 1.25 per cent $BaCO_3$. The quantity of graphite precipitation increased up to 10 per cent $BaCO_3$, beyond which there was no increase apparent. In general, it was observed that the deposition of graphite was not quite so great with $BaCO_3$ as with Na_2CO_3 under similar conditions of temperature and energizer concentration. As the temperature of carburization dropped, the concentration of Na_2CO_3 and $BaCO_3$ required to produce visible deposition of graphite increased. At 800 degrees Cent. (1470 degrees Fahr.) and below, no visible deposit of graphite was secured with 15 per cent $BaCO_3$ present in the compound. At 750 degrees Cent. (1380 degrees Fahr.) and below, no visible deposition of graphite was obtained with 15 per cent Na_2CO_3 present in the mixture.

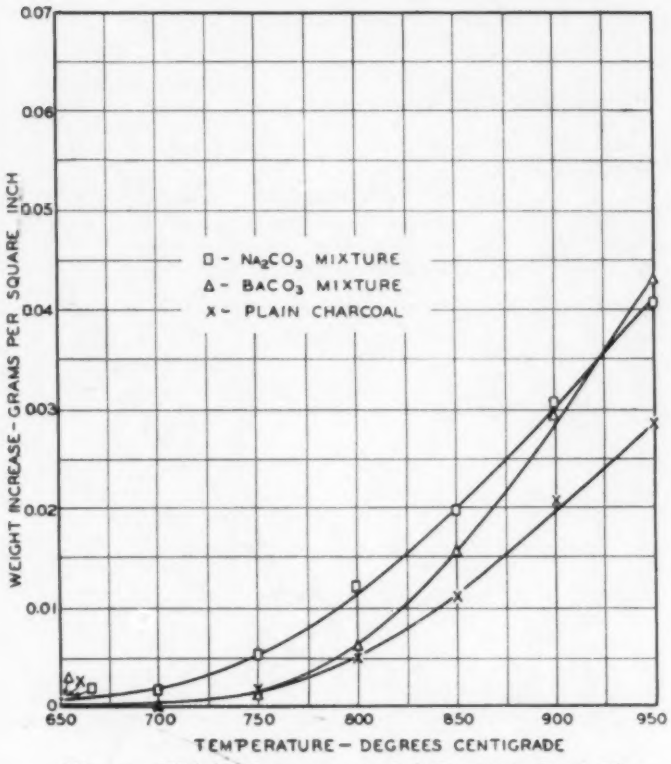

Fig. 1—Weight Increase of S.A.E. 1020 Steel Upon Carburization With 1.25 Per Cent Energizers.

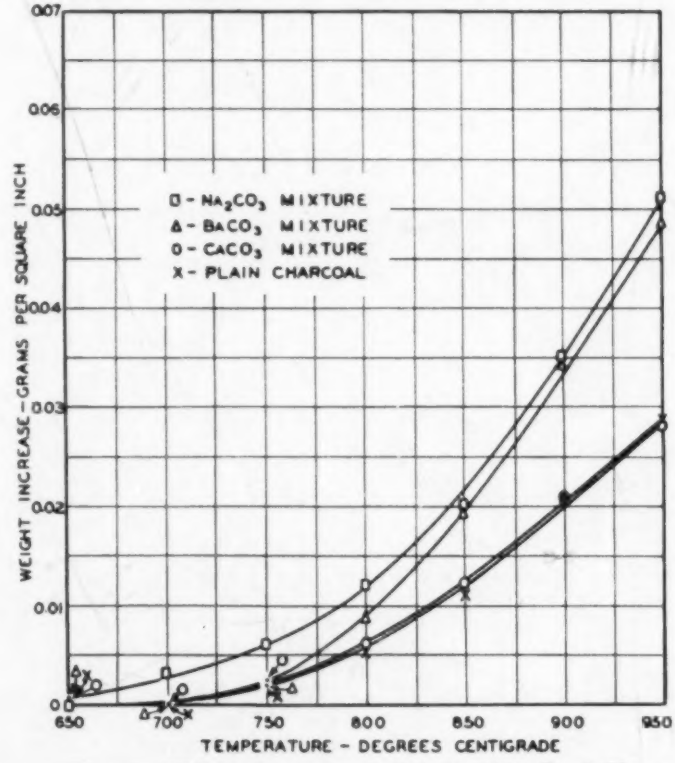

Fig. 2—Weight Increase of S.A.E. 1020 Steel Upon Carburization With 2.5 Per Cent Energizers.

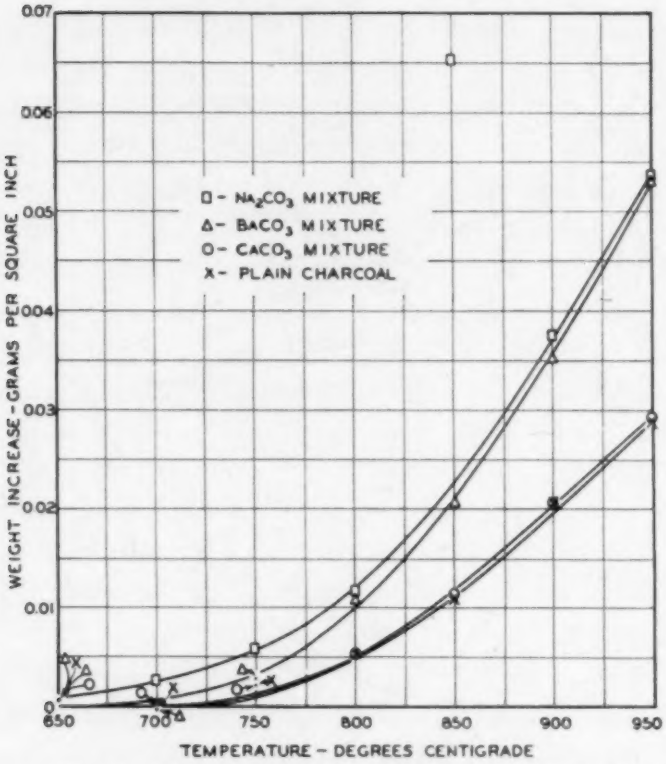

Fig. 3—Weight Increase of S.A.E. 1020 Steel Upon Carburization With 5.0 Per Cent Energizers.

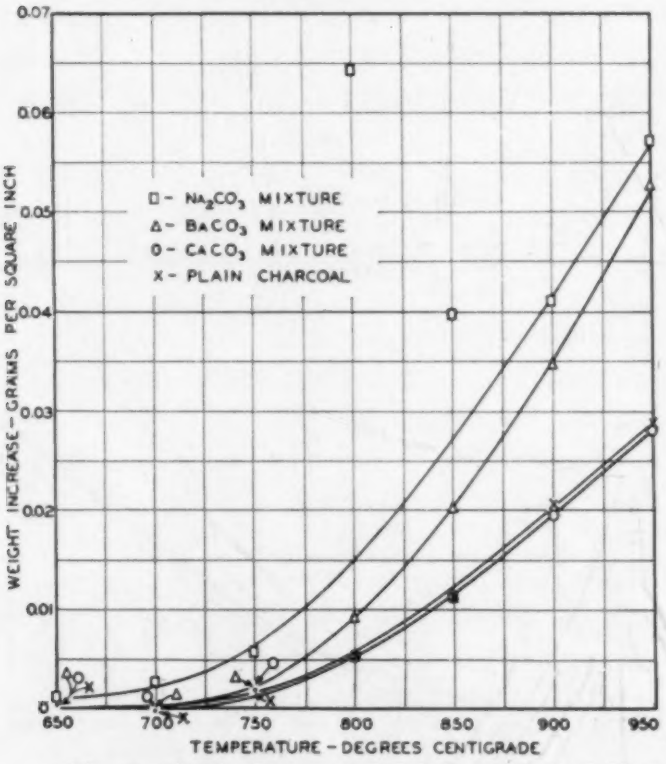

Fig. 4—Weight Increase of S.A.E. 1020 Steel Upon Carburization With 10 Per Cent Energizers.

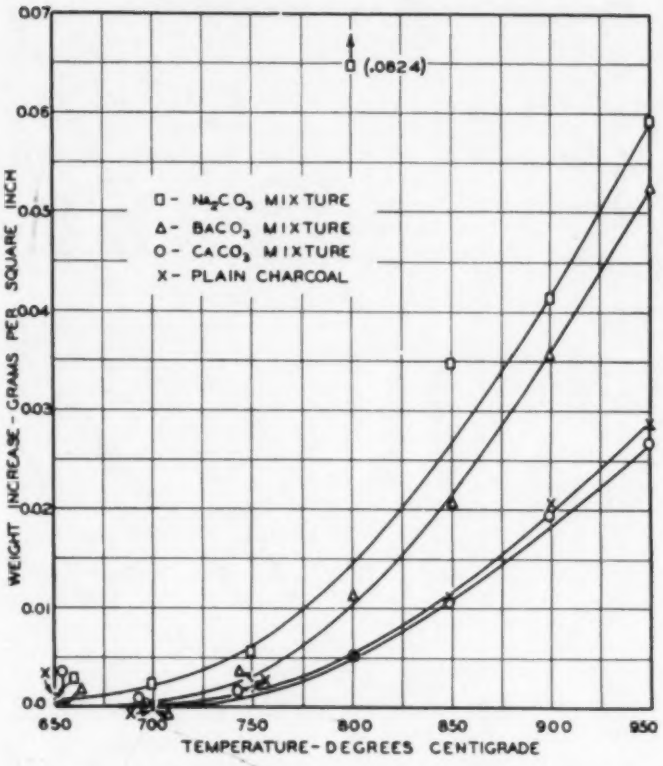

Fig. 5—Weight Increase of S.A.E. 1020 Steel Upon Carburization With 15.0 Per Cent Energizers.

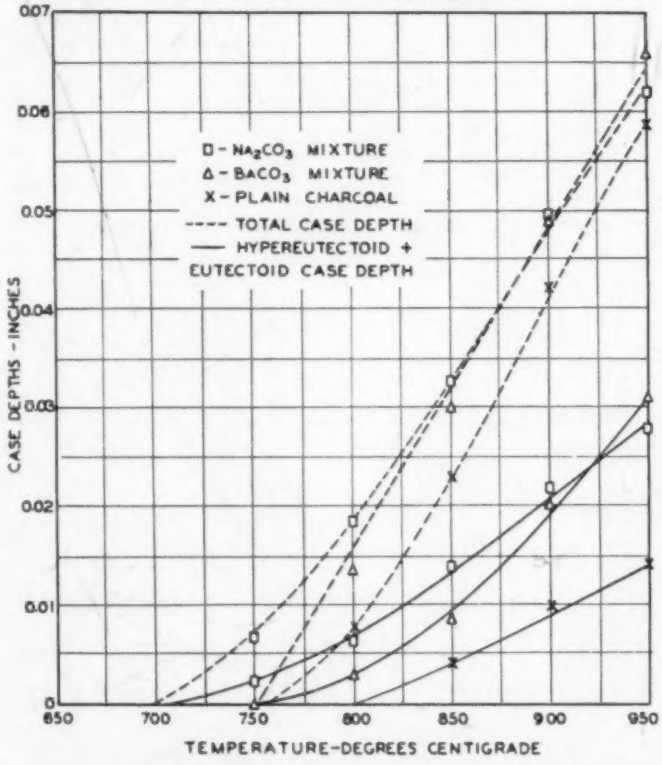

Fig. 6—Depth of Carbon Penetration in S.A.E. 1020 Steel Upon Carburization With 1.25 Per Cent Energizers.

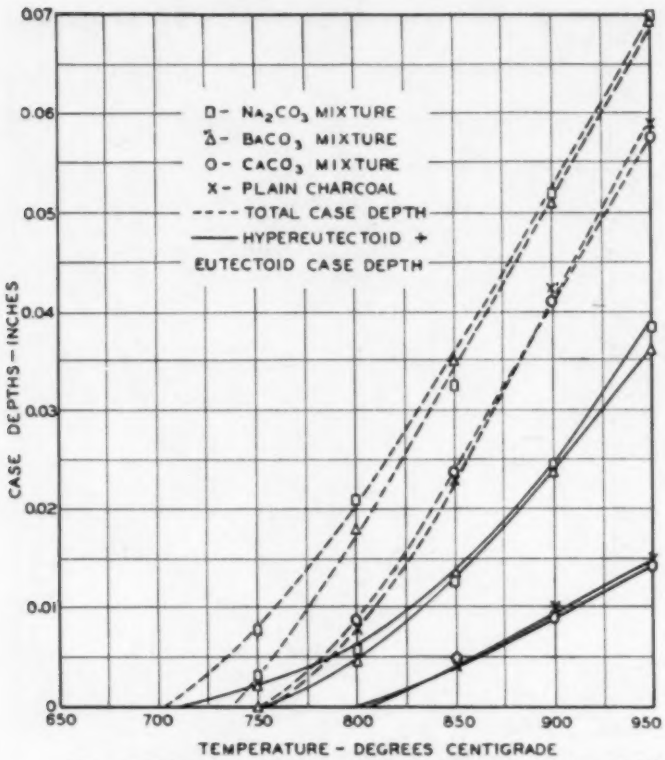

Fig. 7—Depth of Carbon Penetration in S.A.E. 1020 Steel Upon Carburization With 2.50 Per Cent Energizers.

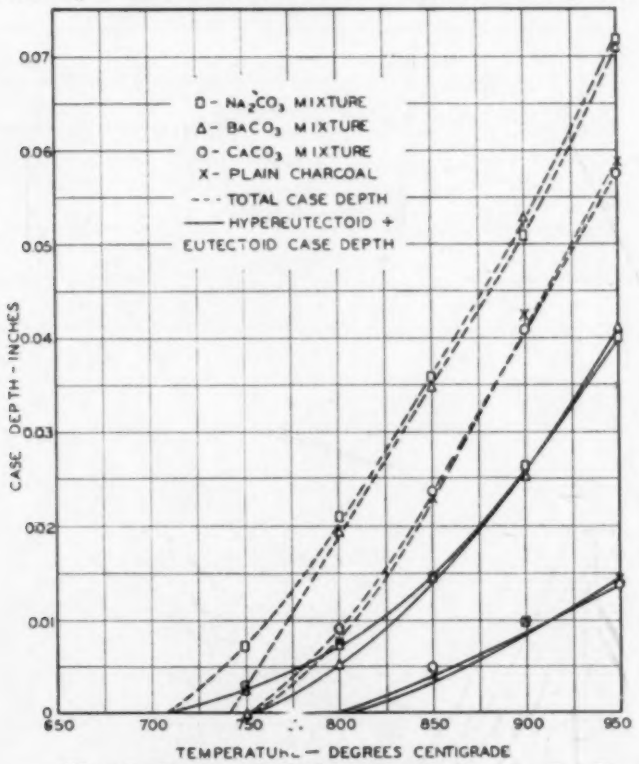

Fig. 8—Depth of Carbon Penetration in S.A.E. 1020 Steel Upon Carburization With 5.00 Per Cent Energizers.

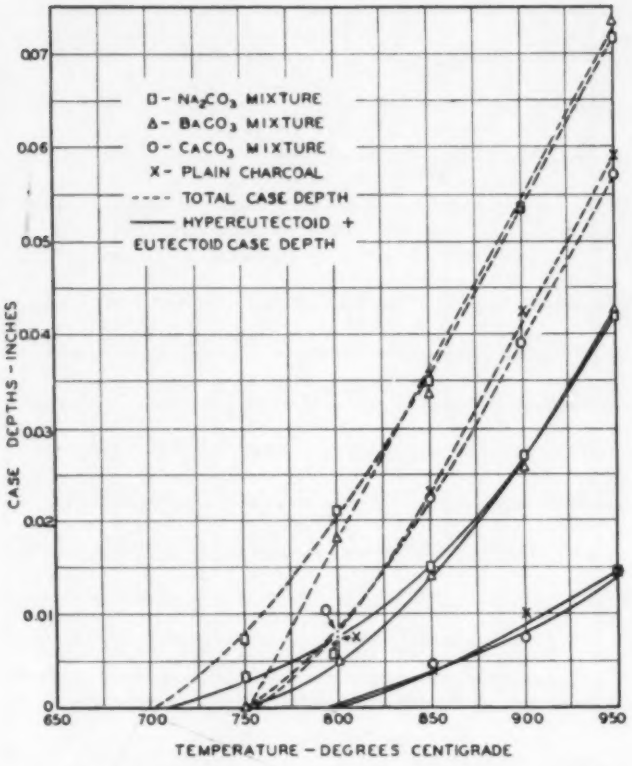

Fig. 9—Depth of Carbon Penetration in S.A.E. 1020 Steel Upon Carburization With 10.00 Per Cent Energizers.

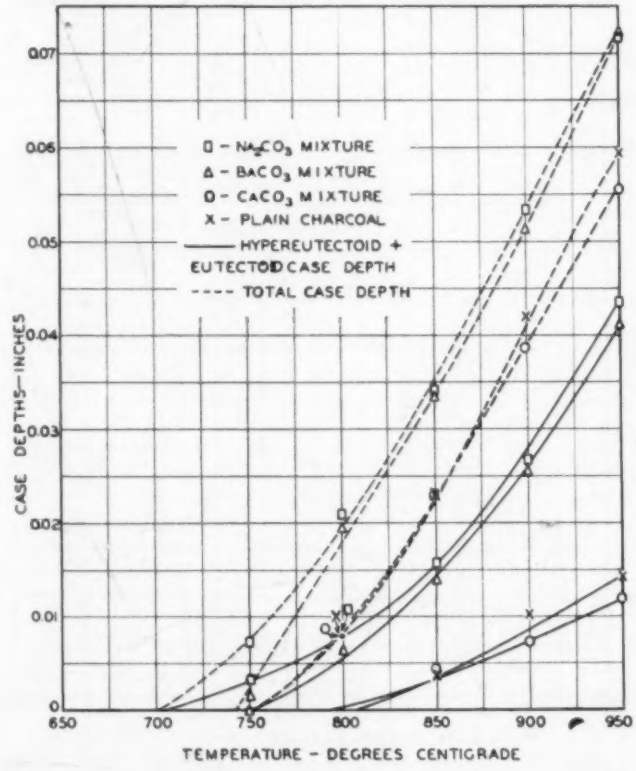

Fig. 10—Depth of Carbon Penetration in S.A.E. 1020 Steel Upon Carburization With 15.00 Per Cent Energizers.

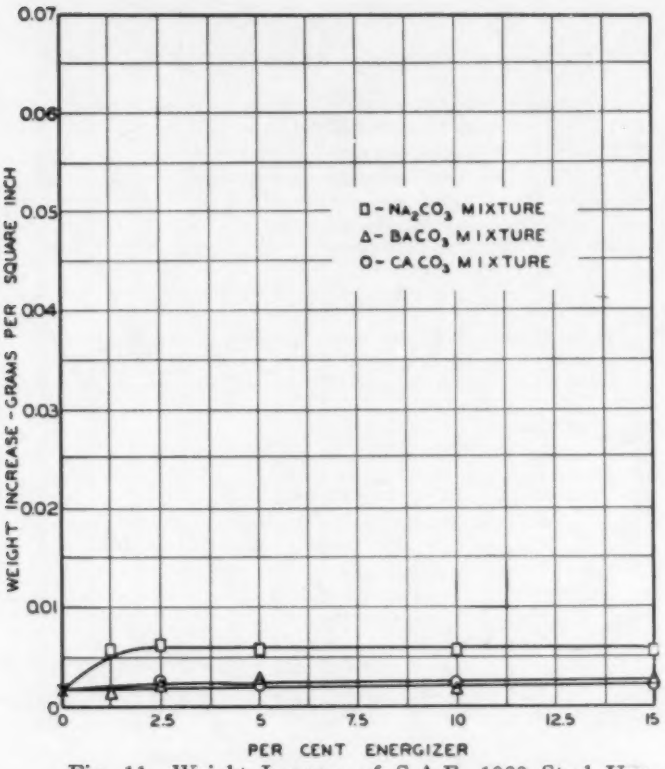

Fig. 11—Weight Increase of S.A.E. 1020 Steel Upon Carburization at 750 Degrees Cent. With Different Concentrations of Energizers.

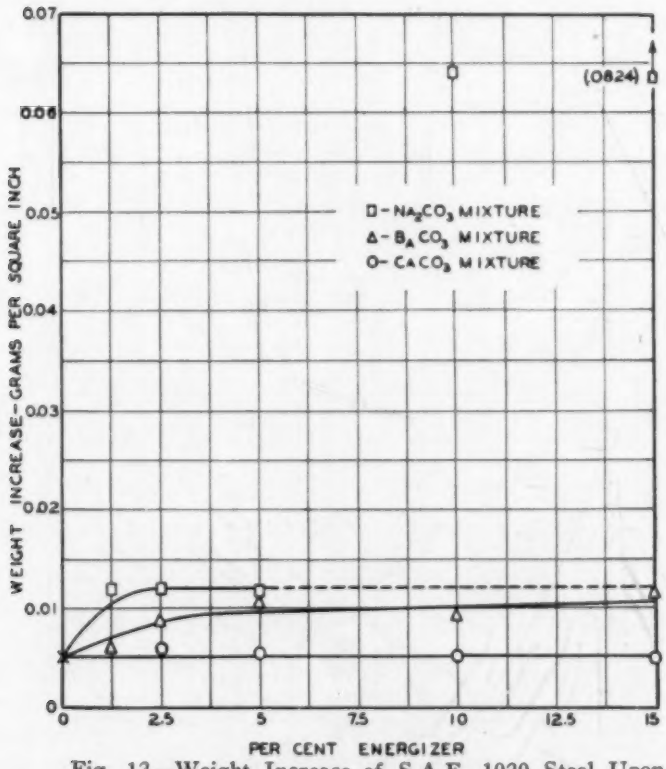

Fig. 12—Weight Increase of S.A.E. 1020 Steel Upon Carburization at 800 Degrees Cent. With Different Concentrations of Energizers.

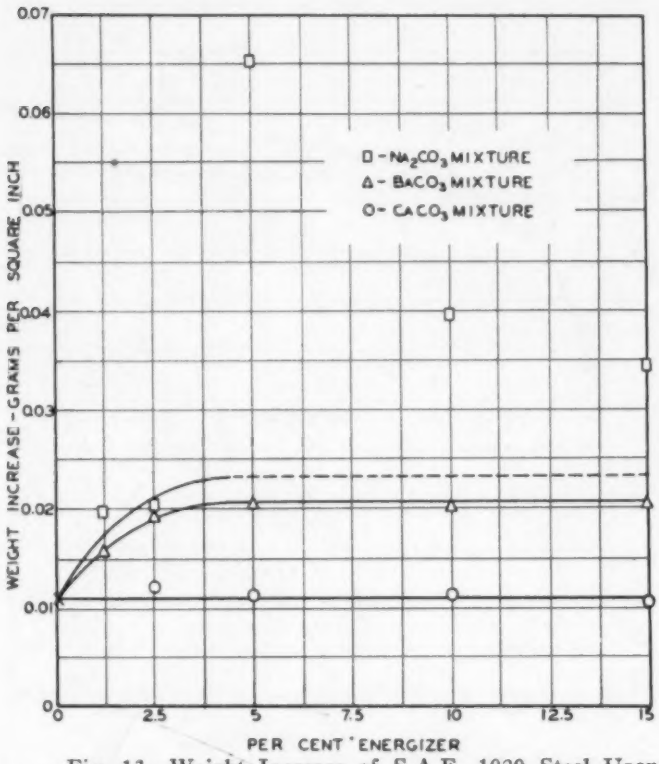

Fig. 13—Weight Increase of S.A.E. 1020 Steel Upon Carburization at 850 Degrees Cent. With Different Concentrations of Energizers.

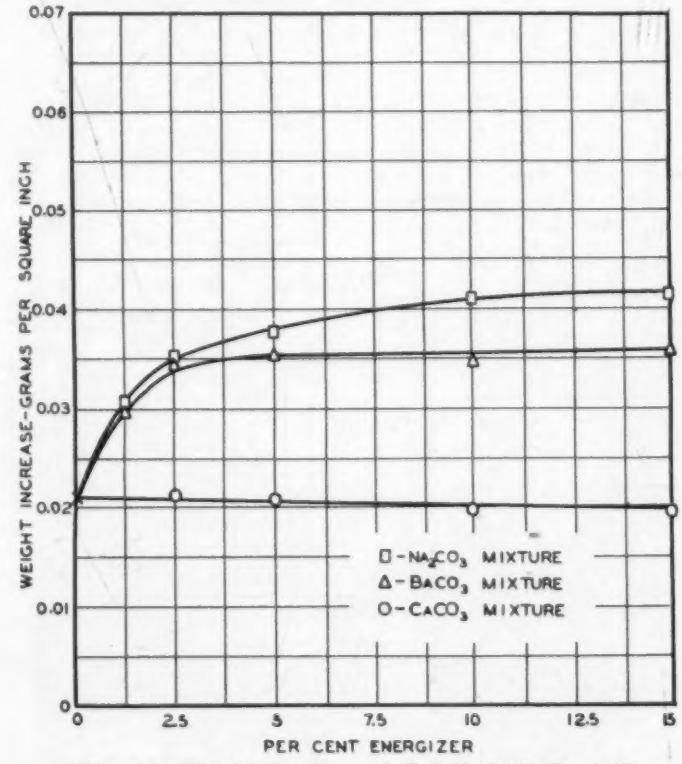

Fig. 14—Weight Increase of S.A.E. 1020 Steel Upon Carburization at 900 Degrees Cent. With Different Concentrations of Energizers.

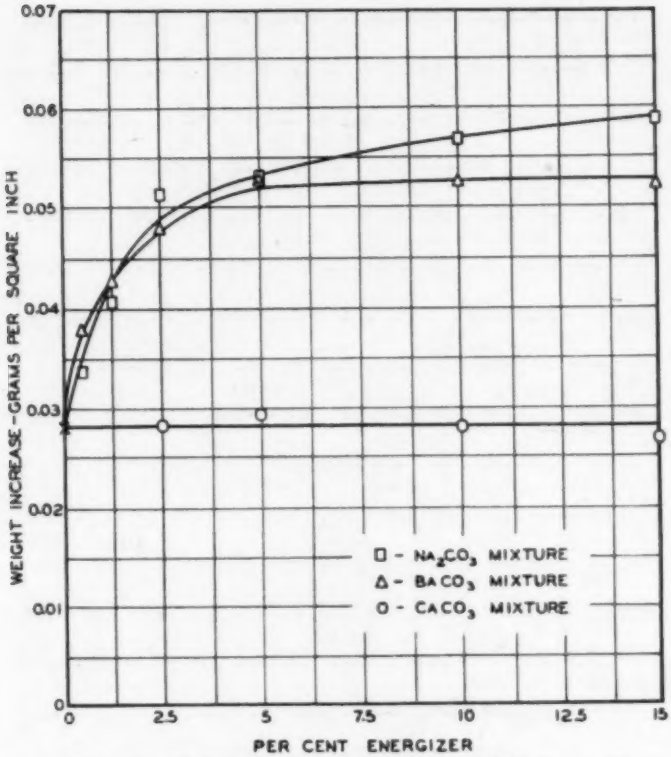

Fig. 15—Weight Increase of S.A.E. 1020 Steel Upon Carburization at 950 Degrees Cent. With Different Concentrations of Energizers.

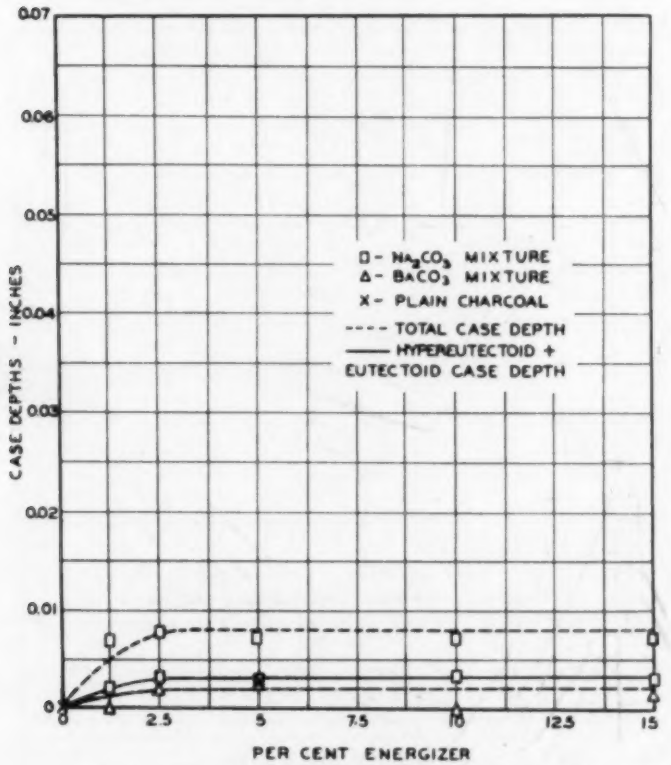

Fig. 16—Depth of Carbon Penetration in S.A.E. 1020 Steel Upon Carburization at 750 Degrees Cent. With Different Concentrations of Energizers.

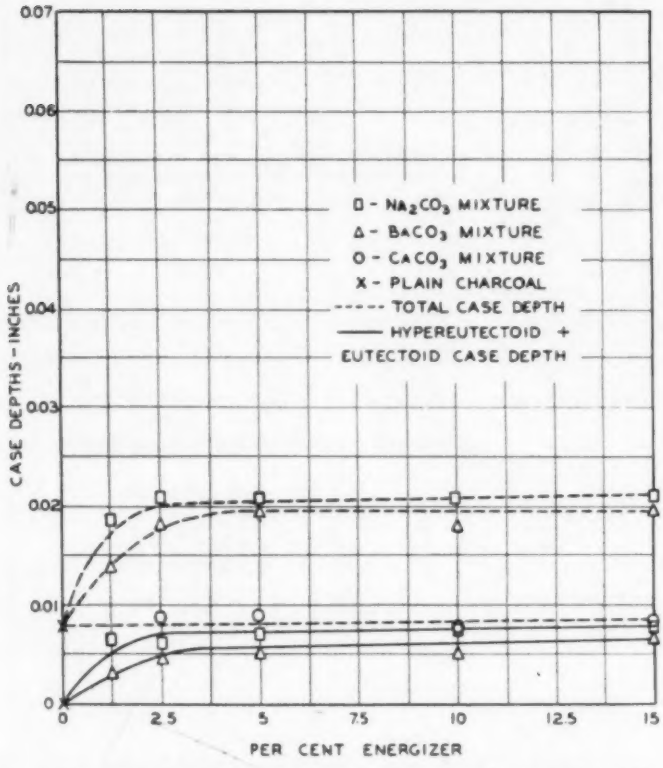

Fig. 17—Depth of Carbon Penetration in S.A.E. 1020 Steel Upon Carburization at 800 Degrees Cent. With Different Concentrations of Energizers.

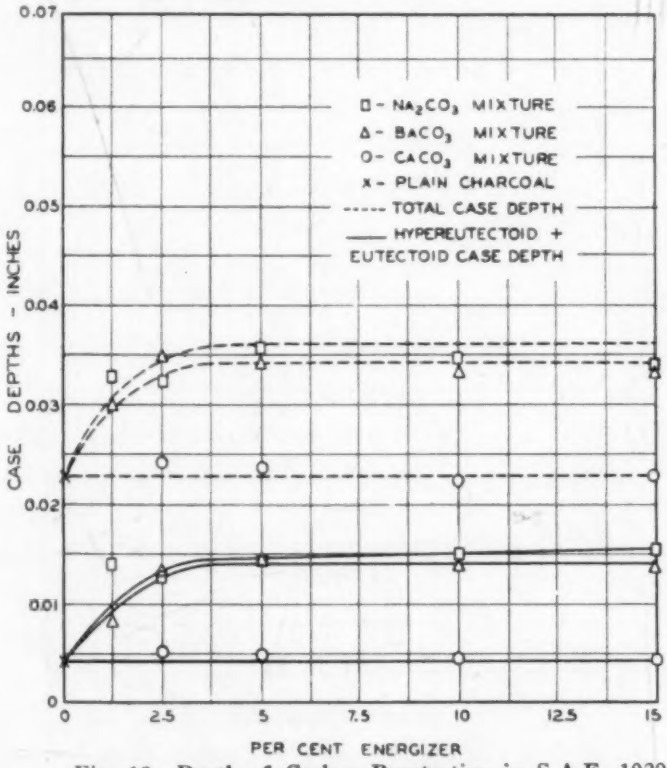

Fig. 18—Depth of Carbon Penetration in S.A.E. 1020 Steel Upon Carburization at 850 Degrees Cent. With Different Concentrations of Energizers.

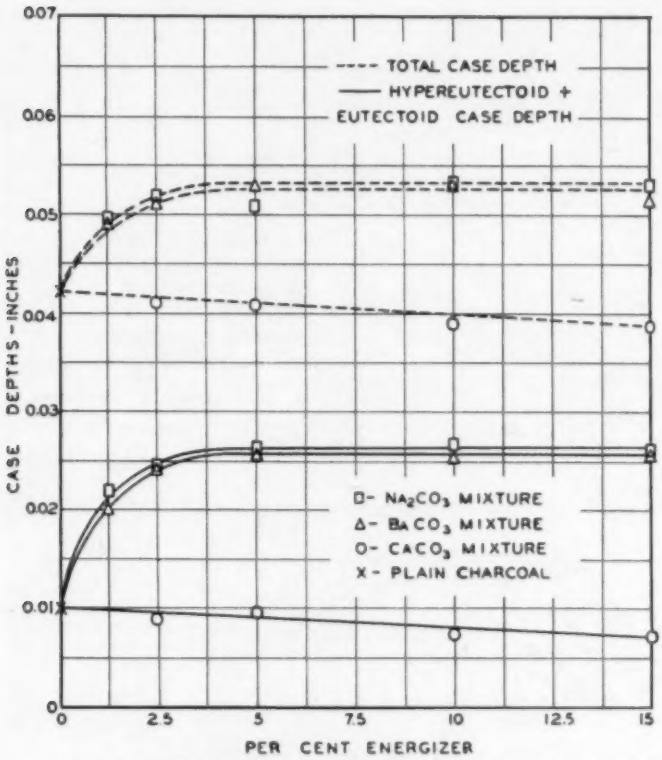

Fig. 19—Depth of Carbon Penetration in S.A.E. 1020 Steel Upon Carburization at 900 Degrees Cent. With Different Concentrations of Energizers.

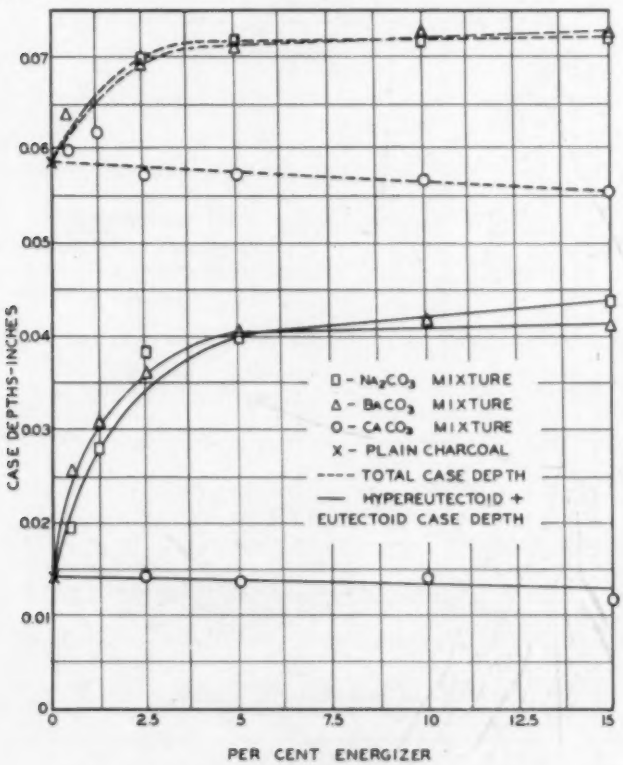

Fig. 20—Depth of Carbon Penetration in S.A.E. 1020 Steel Upon Carburization at 950 Degrees Cent. With Different Concentrations of Energizers.

Since plain charcoal and charcoal mixed with the ineffective $CaCO_3$ produce no visible precipitation of graphite on the steel, and since the extremely active $BaCO_3$ and Na_2CO_3 do induce marked precipitation of graphite, it appears possible that this effect may, in part, be responsible for the accelerated rate of carbon absorption by steel when compounds energized either with $BaCO_3$ or Na_2CO_3 are used.

With most of the samples on which precipitation of graphite occurred it was possible to remove the deposit quite completely. The weight increases of the cleaned specimens were consistent with the case depth measurements and lined up to give smooth curves. In other instances, notably at 800 degrees Cent. (1470 degrees Fahr.) with 10 and 15 per cent Na_2CO_3, and at 850 degrees Cent. (1560 degrees Fahr.) with 5, 10 and 15 per cent Na_2CO_3, the deposit was dense and tightly adherent and could not be removed successfully. In such instances, the weight increases are obviously of no significance as an index of degree of carburization. In drawing the curves shown in Figs. 12 and 13 the curve for Na_2CO_3 beyond about 5 per cent concentration was drawn dotted, as the weight increase values for higher energizer concentrations were high because of graphite deposition. It was assumed that the curves flattened off beyond 5 per cent Na_2CO_3 since the curves for case depth versus Na_2CO_3 concentration exhibited such characteristics.

At 650 degrees Cent. (1200 degrees Fahr.), the specimens heated in plain charcoal or in charcoal mixed with $BaCO_3$ or $CaCO_3$ all exhibited a darkened surface appearance. The ready solubility of this coating in dilute acid indicated that the surface was covered by a film of oxide, rather than of graphite. Samples heated at 650 degrees Cent. (1200 degrees Fahr.) in a mixture containing Na_2CO_3 as energizer exhibited bright, clean surfaces, free from an oxide coating.

From the foregoing comments and from a study of the graphs, the following observations may be made.

1. Calcium carbonate is entirely inert as an energizer for hardwood charcoal. It seems to be merely an inert diluent.

2. Both Na_2CO_3 and $BaCO_3$ are powerful energizers when used with hardwood charcoal and give results of the same order of magnitude. The Na_2CO_3 appears to give a slightly greater effect when operating at the high temperatures normally used in carburizing operations. It is interesting to note that the Na_2CO_3 imparts a

definite energizing action even at the lower temperatures of 750, 700 and 650 degrees Cent. (1380, 1290, 1200 degrees Fahr.), whereas $BaCO_3$ is practically without effect.

3. The curves of Figs. 11 to 20 show that there is little to be gained by increasing the concentration of energizer beyond 5 per cent Na_2CO_3 or 5 per cent $BaCO_3$. The curves flatten off between 2½ and 5 per cent and show relatively little increase beyond 5 per cent.

Figs. 1 to 20 show very completely the manner in which degree of carburization is influenced by temperature and energizer concentration, when working with hardwood charcoal energized with $BaCO_3$, $CaCO_3$ or Na_2CO_3.

Relative Effectiveness of Various Carbonaceous Materials When Using Barium, Calcium and Sodium Carbonates as Energizers

While it is well recognized that various carbonaceous substances differ in their capacity to carburize steel, quantitative data are scant, particularly so with reference to their relative effectiveness when energized with barium, calcium or sodium carbonates. Coke is frequently used as a component of commercial carburizers, even though it is recognized that the coke does not posses the inherent capacity to carburize that charcoal does. The presence of coke is justified on the grounds that it reduces shrinkage in use and improves thermal conductivity. McQuaid (7) in the recent carburizing symposium briefly considered the question of relative activity of various types of carbonaceous materials and stated that energized lamp black would not carburize at a commercially satisfactory rate. Charcoal gave results far superior to broken arc lamp carbons, graphite and coke, though no statement was made whether this merely applied to the unenergized materials, or to the materials after normal additions of energizing agents had been made.

In the present investigation, the following carbonaceous substances were used: (a) Hardwood charcoal of the same type as previously used. (b) Preheated hardwood charcoal. This material was the same as previously used, but prior to use it was heated in the standard carburizing retorts for one hour at 950 degrees Cent. (1740 degrees Fahr.) in order to drive off volatiles. The average loss in weight observed in this operation was 23.4 per cent. (c) Sugar

Table I
Moisture and Ash Content of the Carbonaceous Substances

Carbonaceous Substance	Per Cent Moisture	Per Cent Ash Moisture-Free Basis	Reaction to Hot Dilute HCl
Hardwood Charcoal	2.48	3.30	Readily soluble
Preheated Hardwood Charcoal	0.20	4.00	Readily soluble
Sugar Charcoal	0.24	0.40	Insoluble
Acheson Graphite	0.00	0.03	Insoluble
Carbon Black	1.33	0.05	Insoluble
Retort Carbon	0.06	2.53	Insoluble
Metallurgical Coke	0.05	7.38	Partly soluble

charcoal, made from pure cane sugar. The sugar was first reduced to a charred mass by heating in Pyrex glass beakers, and was finally heated one hour at 950 degrees Cent. (1740 degrees Fahr.) in the standard carburizing retorts. (d) Acheson graphite. (e) Carbon black. (f) Retort carbon. (g) Metallurgical coke.

The graphite and carbon black were in finely divided form as purchased and were given no additional grinding before use. The other materials were reduced to powdered form before use.

Ash determinations were made on all of the carbonaceous substances, since it has been pointed out by several investigators that the alkaline ash normally found in charcoal may be responsible at least in part for the rather marked carburizing power of unenergized charcoal. While it was not feasible to analyze the ash residues, a qualitative test was made of them with hot dilute hydrochloric acid. Those ash residues that are high in alkali and alkaline earth oxides will dissolve readily, whereas a condition of insolubility may be considered as indicating the absence of appreciable amounts of alkali and alkaline earth oxides. Results of these tests are given in Table I.

All mixes used in the experimental work contained 90 per cent of the carbonaceous substance (on a dry basis) and 10 per cent of the dry energizer. The standard carburizing cycle of 7 hours at 950 degrees Cent. (1740 degrees Fahr.) followed by air cooling of the retorts was adhered to.

The data obtained are summarized in Table II. A study of the figures in this table lead to the following conclusions.

1. Considering first the unenergized compounds, it is apparent that the three charcoals were far superior to the other materials. The preheated charcoal exhibited a somewhat lower degree of activity than the fresh charcoal, presumably due to the loss of volatile

Table II

Summarized Data of Carburization Produced by Different Carbon Bases

Carbon Base	Measurment	Energizer Na_2CO_3	Energizer $BaCO_3$	Energizer $CaCO_3$	Plain Carbon Base
Hardwood Charcoal 14-A	WT. I.	0.0540	0.0484	0.0270	0.0287
	HE. + E.	0.0391	0.0364	0.0112	0.0124
	T. D.	0.0695	0.0685	0.0569	0.0564
Preheated Charcoal 14-AH	WT. I.	0.0509	0.0504	0.0244	0.0244
	HE. + E.	0.0392	0.0389	0.0072	0.0079
	T. D.	0.0700	0.0699	0.0471	0.0520
Sugar Charcoal S-2	WT. I.	0.0516	0.0506	0.0241	0.0203
	HE. + E.	0.0407	0.0398	0.0078	0.0053
	T. D.	0.0714	0.0699	0.0516	0.0494
Acheson Graphite AG	WT. I.	0.0393	0.0353	0.0018	0.0036
	HE. + E.	0.0300	0.0209	nil	nil
	T. D.	0.0665	0.0638	nil	0.0042
Carbon Black Ce	WT. I.	0.0506	0.0452	0.0094	0.0082
	HE. + E.	0.0394	0.0347	nil	nil
	T. D.	0.0678	0.0672	0.0288	0.0310
Retort Carbon 13	WT. I.	0.0452	0.0113	0.0079	0.0027
	HE. + E.	0.0350	nil	nil	nil
	T. D.	0.0694	0.0298	0.0093	nil
Metallurgical Coke FC	WT. I.	0.0353	0.0434	0.0311	0.0029
	HE. + E.	0.0208	0.0322	0.0133	nil
	T. D.	0.0628	0.0683	0.0642	nil

WT. I. Average weight increase upon carburization; expressed in grams per square inch of surface area of specimen.

HE. + E. Average hypereutectoid plus eutectoid case depth for specimen; expressed in inches.

T. D. Average total case depth of specimen; expressed in inches.

hydrocarbons in the preheating operation. The sugar charcoal possessed the lowest activity of the three charcoals, but was far superior to the other materials. The Acheson graphite, carbon black, retort carbon and metallurgical coke, while not entirely inert, nevertheless carburized very slowly as compared to the charcoals.

2. The calcium carbonate appears to be entirely inert except in one unique case—when mixed with the metallurgical coke. Here it acts as an extremely effective energizer though it still is not equal in its effects to barium or sodium carbonate. While no experimental work was performed with the objective of explaining the mechanism whereby calcium functions as a successful energizer with coke, the following tentative hypothesis is advanced. An examination of typical ash analyses for coals from a great variety of sources (8) indicates that the major components of the ash are SiO_2, Al_2O_3 and Fe_2O_3. These oxides presumably do not exist in the free, uncombined state, neither in the ash, nor in the original coal, nor in the coke made from the coal. It is quite probable that the bulk of the iron exists in the form of sulphides and silicates in the original coal, and also in the coke made from the coal. In such form, the iron is ineffective as an energizer. The addition of $CaCO_3$ to the coke

provides a powerful basic material which probably combines with the sulphur and the silica, thus releasing the iron from combination. It is believed that the release of the iron, which will exist in the metallic state and in finely divided form under carburizing conditions, is of significance, for it has been shown (9) that finely divided metals, such as iron and nickel, are capable of exerting well defined energizing effects. As a matter of fact, Rodman (10) finds that it is possible to prepare an extremely active carburizing compound using only Fe_2O_3 and $CaCO_3$ as energizers, omitting entirely the usual energizers such as $BaCO_3$ and Na_2CO_3.

3. Sodium carbonate is an extremely effective energizer with all of the carbonaceous substances.

4. Barium carbonate is very effective except with one material, retort carbon, with which it exerts an extremely weak energizing effect. It is probable that the barium carbonate reacts with the ash and is rendered largely ineffective.

5. In most instances, barium and sodium carbonates produce effects of the same order of magnitude, with the sodium carbonate usually slightly the better of the two. With metallurgical coke, however, the order of merit is reversed, with the barium carbonate being the better.

6. While preheating of the hardwood charcoal definitely reduces its activity when no energizer is used, the results show that when barium or sodium carbonates are added, little or no reduction in carburizing rate results from preheating.

7. Some of the other mixes, notably those of sugar charcoal with sodium or barium carbonate and carbon black with sodium carbonate, closely approach the activity of the fresh charcoal energized with the corresponding carbonate.

8. Some of the data appear to indicate that there are inherent differences in the carburizing ability of pure carbonaceous substances, that persist even after additions of energizer have been made. For example, both carbon black and Acheson graphite have very low ash contents and are rather pure forms of carbon. Without energizer both possess a very low activity, with the carbon black somewhat the better. Energizing with either sodium or barium carbonate produces a tremendous increase in activity with both substances, but the compounds made with carbon black are still superior to those made with Acheson graphite.

9. A definite correlation was observed between the precipita-

tion of graphite on the surfaces of the steel specimens and the degree of carburization. Those compounds producing a high degree of carburization caused the precipitation of graphite on the surfaces of the specimens. The hardwood charcoal, the preheated charcoal and the sugar charcoal all yielded well defined graphite deposits when barium carbonate and sodium carbonate were used. The deposition of graphite was most noticeable when using sodium carbonate. Carbon black, when energized with sodium carbonate, also produced graphite deposition. The compounds other than those noted exhibited a lesser degree of activity, and they produced no precipitation of graphite on the steel surfaces.

Changes in Carburizing Compounds on Use

Apparent Loss of Energizer and Its Relation To Carburizing Activity—A series of experiments was performed with the object of determining whether any significant loss of the sodium, barium or calcium present in the original energizer chemicals occurred in use. In the course of this investigation it was discovered that in certain instances those extraction procedures which were capable of effecting complete recoveries when applied to the unused carburizing compounds failed to give complete recoveries after use. The apparent losses in some instances were very great, at times being in excess of 50 per cent of the metal content of the original energizer present in the compound. Such apparent losses were only encountered with the carbonates of sodium and barium, which are extremely active as energizers. When working with calcium carbonate, which is ineffective as an energizer, the recoveries of calcium ran at practically 100 per cent.

Further investigation showed that the losses encountered when working with sodium and barium carbonates as energizers were apparent, not real, losses. The residues from the normal extraction procedures were ashed down at a low temperature, and when the ashes were extracted, practically complete recoveries of the sodium and the barium were obtained.

In performing the experimental work, hardwood charcoal of the type previously used was employed. The mixes all contained 90 per cent charcoal and 10 per cent energizer, and were subjected to the standard cycle of 7 hours at temperature, followed by air cooling of the retorts. Each retort contained two of the stand-

ard steel specimens, which were used to evaluate the degree of carburization. Temperatures ranged from 950 to 650 degrees Cent. (1740 to 1200 degrees Fahr.) in steps of 50 degrees Cent. Other details of experimental procedure were as described previously.

Experimental results are plotted in Figs. 21 to 23. The figures show that with calcium carbonate as energizer, the calcium loss is practically nil under all conditions, and it is also apparent that the calcium carbonate is entirely inert as an energizer. The data and curves for barium carbonate indicate a continuously increasing apparent loss as the temperature rises. In considering the degree of carburization as indicated by weight increases and case depth measurements, it is evident that at low temperatures, where apparent loss is low, the barium carbonate is relatively ineffective as an energizer while at higher temperatures, where apparent losses are high, the barium carbonate is a very effective energizer. The data and curves for sodium carbonate indicate well defined apparent losses at temperatures as low as 650 degrees Cent. (1200 degrees Fahr.) and as the temperature rises, the apparent losses achieve high values. The curve is not a continuously increasing function, but exhibits a well defined maximum at 800 degrees Cent. (1470 degrees Fahr.). The data and curves for weight increases and case depth clearly indicate that sodium carbonate exerts a well defined energizing action at all temperatures investigated.

The steel surfaces were scrutinized after each carburizing treatment, and it was again observed that graphite precipitation occurred when using sodium or barium carbonates as energizers at sufficiently high temperatures. With sodium carbonate at 850 degrees Cent. (1560 degrees Fahr.) the deposit of graphite was so heavy that it could not be removed completely. The weight increases at this temperature are accordingly of no significance for the compound energized with sodium carbonate.

Since graphite precipitation is observed with the carbonates of sodium and barium but not with calcium carbonate, and since apparent losses are obtained with sodium and barium carbonates but not with calcium carbonate, it was concluded that the apparent losses observed can be explained on the basis of the precipitated graphite forming a coating over some of the energizer particles, thus rendering them immune from solution in the extracting fluid. It may be remarked in passing that the coating over the energizer particles must be quite dense and impervious. When working with

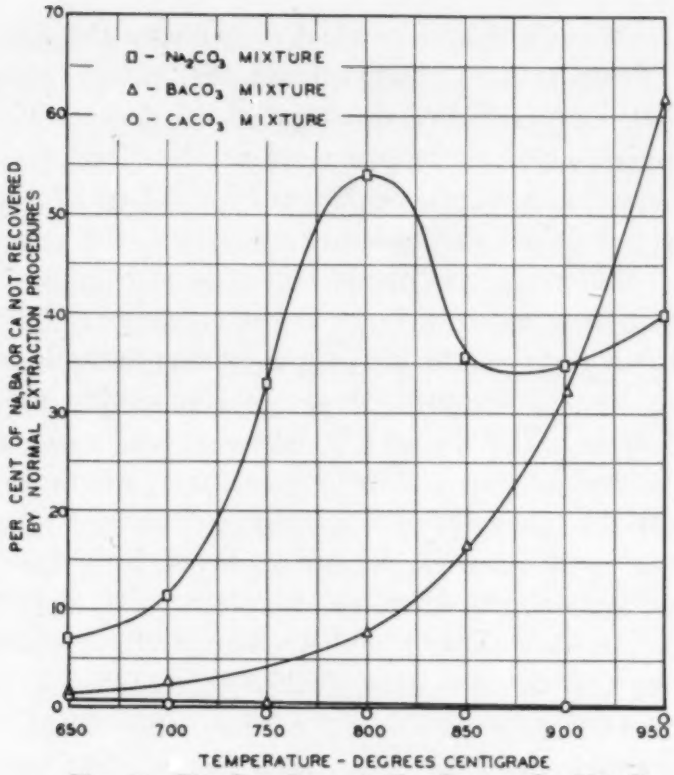

Fig. 21—The Per Cent of N_A, B_A, or C_A Not Recovered by Normal Extraction Procedures, Versus Temperature.

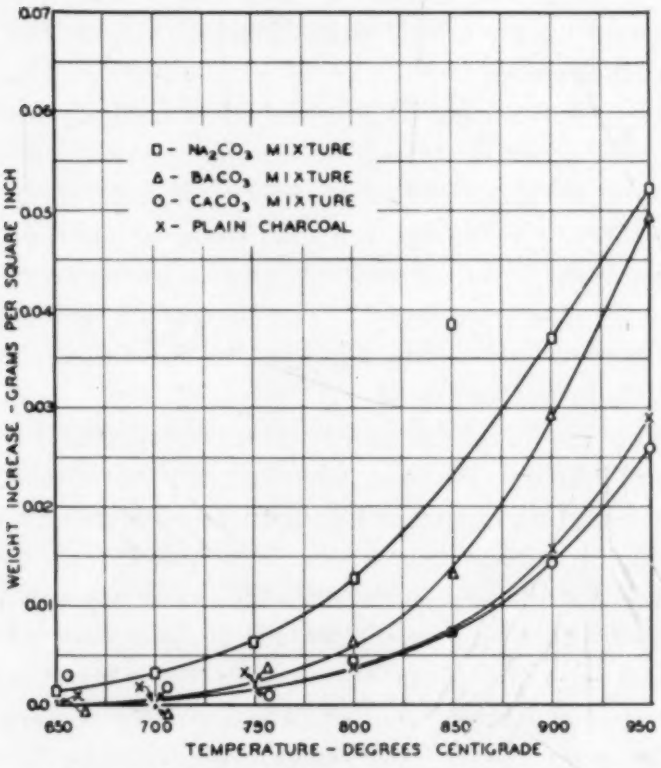

Fig. 22—Weight Increase of S.A.E. 1020 Steel Upon Carburizing With 10.0 Per Cent Energizer.

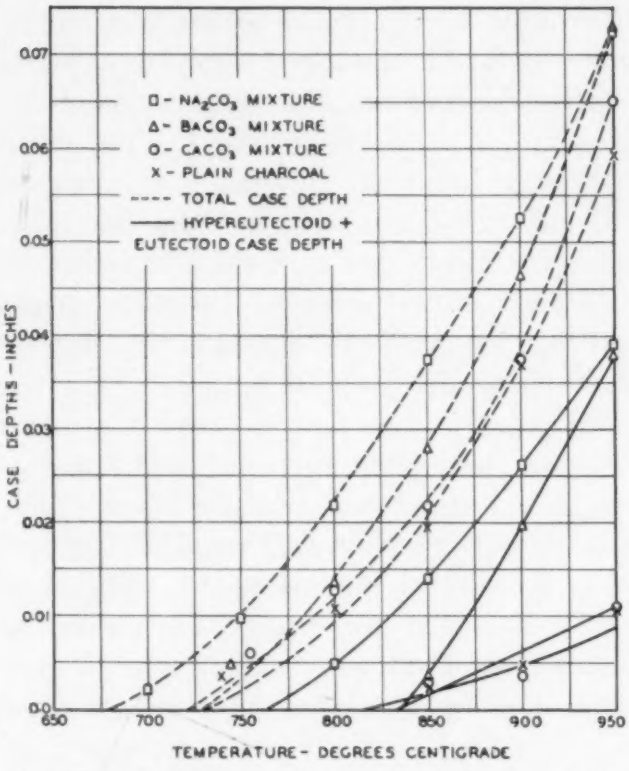

Fig. 23—Depth of Carbon Penetration in S.A.E. 1020 Steel Upon Carburization With 10.00 Per Cent Energizers.

barium energized compounds, it was observed that the application of a third extraction treatment with hot dilute hydrochloric acid, in addition to the two extractions normally used, produces an extract that reacts entirely negative when tested qualitatively for barium. Yet on ashing down the residue, the remainder of the barium is recovered. When working with a sodium energized compound, the application of extraction treatments in excess of the two normally used resulted in a very slight, though definite, pick-up of alkali.

It appears that there is a definite correlation between the capacity of a material to accelerate the absorption of carbon by steel, its tendency to induce graphite precipitation, and the apparent loss of energizer sustained in use.

The question may be raised whether or not the energizer trapped by the precipitated graphite is entirely inert, or whether it can exert a catalytic effect when the compound is used subsequently. Several tests were carried out, in which a compound was used for three successive carburizing treatments. After each treatment, the normal

extraction procedures were applied to the compound, thus leaving in the compound only the entrapped energizer. After the wet extraction and before further use, the mixtures were dried completely at 105 degrees Cent. (220 degrees Fahr.). The carbonaceous base was powdered sugar charcoal, prepared as previously indicated. Sodium and barium carbonates were used as energizers, and the carburizing mixes contained 90 per cent sugar charcoal and 10 per cent energizer at the start of the series of three carburizing treatments. The normal carburizing cycle of 7 hours at 950 degrees Cent. (1740 degrees Fahr.) was applied in each instance. The results are plotted in Figs. 24 and 25. The figures given for per cent energizer were obtained by computing the carbonate equivalent of the retained energizer, even though it was not actually in carbonate form.

The curves indicate that the sodium is not rendered ineffective, even in the second re-use of the compound. The barium carbonate, however, behaves somewhat differently. On the re-use for the first time, the residual barium still exerts a positive effect, but on second re-use it seems to be entirely inert, even though the concentration, computed as carbonate, is some 5 per cent, which is high enough to produce a pronounced degree of activity in a fresh compound.

Decomposition of Carbonate in Use—A few scattering tests were made on the completeness of carbonate decomposition at the completion of the normal carburizing cycle at 950 degrees Cent. (1740 degrees Fahr.). These tests, few and incomplete as they are, indicate that when using sodium carbonate as energizer, the extractable alkali is almost completely in hydroxide form, indicating practically complete decomposition of the carbonate after 7 hours at 950 degrees Cent. (1740 degrees Fahr.). Further study is being made of the rate of carbonate decomposition in carburizing compounds.

Decline in Activity When Used—While it is universally recognized that a carburizing compound declines in activity on use, quantitative data on the degree to which the carburizing activity declines on repeated use are relatively scarce.

In this portion of the investigation, the carburizing compounds were used for three successive carburizing treatments, without the addition of any fresh material. The carbonaceous base selected was hardwood charcoal of the type previously described. Carbonates of calcium, barium and sodium were used as energizers, and a concentration of 2.5 per cent energizer in the carburizing compounds was

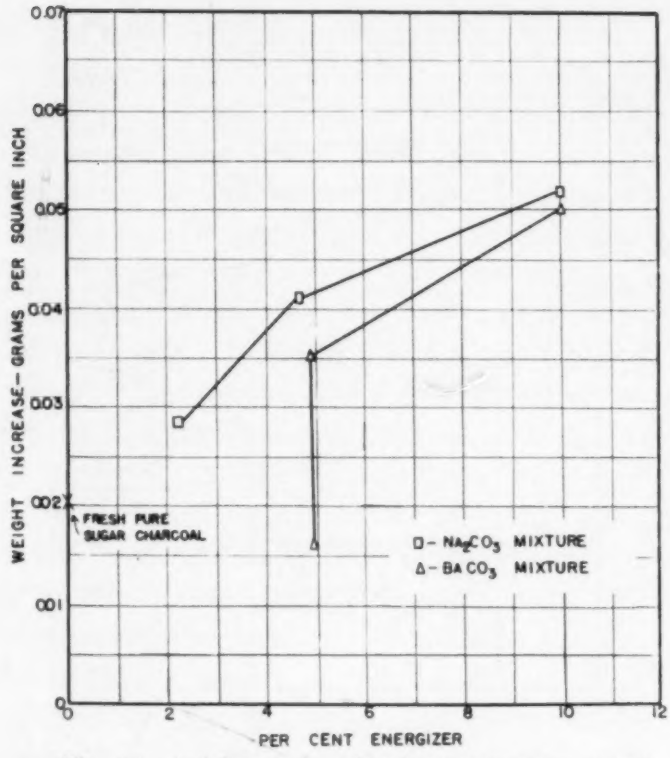

Fig. 24—Activity of the "Retained" Energizer at 950 Degrees Cent.

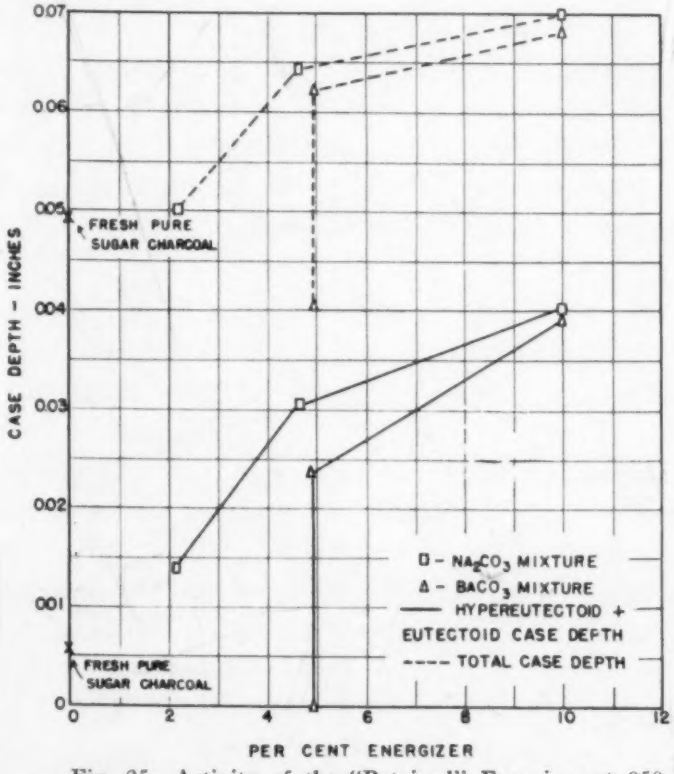

Fig. 25—Activity of the "Retained" Energizer at 950 Degrees Cent.

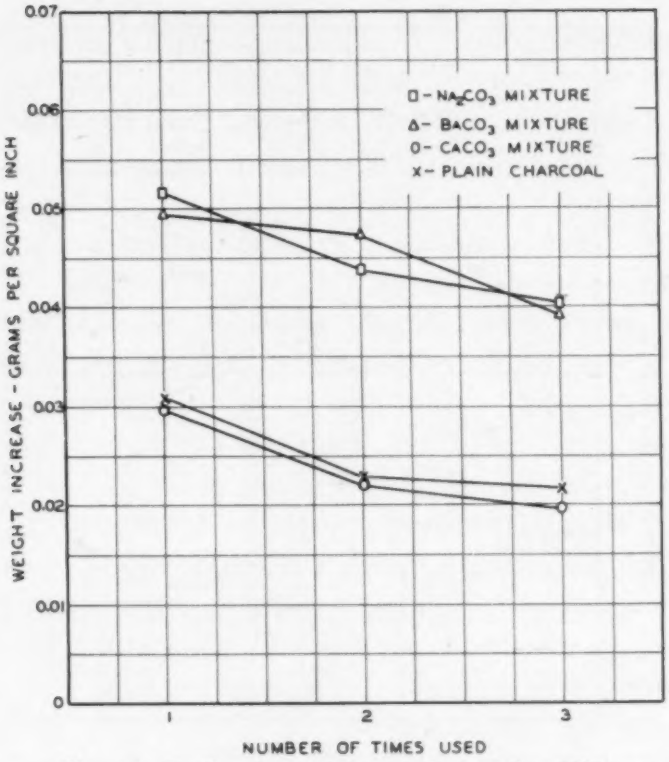

Fig. 26—Decline in Activity of Carburizing Mixtures With Use.

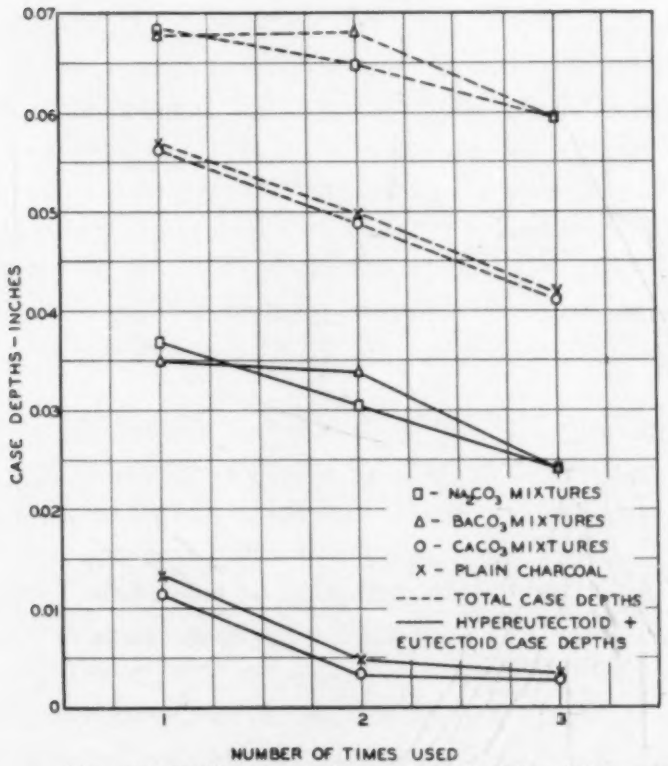

Fig. 27—Decline in Activity of Carburizing Mixtures With Use.

chosen for these tests. In the curves of Figs. 1 to 20 is shown the relation of energizer concentration with carburizing activity, and it is apparent that a rapid decline occurs below 2.5 per cent. The selection of this energizer concentration will accordingly make it easier to recognize a loss in the effectiveness of the energizer than if a higher concentration, say 15 per cent, were selected.

Four retorts were packed with the same carburizing mix, and the assembly of four retorts was then subjected to the standard carburizing cycle involving 7 hours at 950 degrees Cent. (1740 degrees Fahr.) followed by air cooling. After the retorts were cool, they were emptied, and the residue was used to pack two retorts for the second carburizing test. The residue from the second carburizing test was used to pack one retort for the third and final test. It was necessary to use fewer retorts in each succeeding run because of the shrinkage in volume of the carburizing compound.

The results are given in Figs. 26 and 27.

In addition to the numerical data summarized in the graphs, note was taken of the precipitation of graphite on the surfaces of the steel specimens. All of the samples treated with compounds energized with sodium carbonate or barium carbonate exhibited a dark, smooth condition due to deposition of graphite. This applied to the samples prepared in the second and third runs as well as those prepared in the first runs, though it appeared that the first runs produced the greatest deposition of graphite. The samples treated with plain charcoal, or with charcoal to which calcium carbonate had been added, exhibited clean, bright surfaces, entirely free from graphite.

The data indicate a loss in weight of approximately 25 per cent in the first run, regardless of the energizer used. In the second and third runs, the losses were far smaller, and they were all of approximately the same magnitude.

Considering first the results obtained with plain charcoal and with charcoal to which calcium carbonate had been added, a definite decline is noted in the second run, which may reasonably be attributed to the driving off of volatiles. Considering the weight increase data and the data for depth of hypereutectoid plus eutectoid case, which offer the most reliable index of carburizing power, the third run shows a further decline, but it is small in magnitude compared to the decline exhibited in the second run, indicating that the material has reached a fairly constant degree of activity.

In considering the results for the mixes energized with sodium carbonate and barium carbonate, a continual decline in carburizing power is exhibited. In comparing the results of the second run with those from the first run, the situation is complicated by several factors coming into play. The loss of some 25 per cent volatile matter tends to increase the energizer concentration, thus tending to produce an acceleration in carburizing rate. However, the loss of volatile matter in itself represents a loss in carburizing capacity. In addition, some of the energizer particles tend to become coated with graphite and thus some loss in activity is experienced. In comparing the results of the third run with those of the second run, the situation is not so complicated. The slight loss in weight in the second run produces but slight increase in energizer concentration for the third run, hence, we may say that for the second and third runs, energizer concentration is practically identical. The fact that a well defined drop in activity is exhibited in the third run as compared to the second run seems to indicate a definite loss in effectiveness of the energizer. This may be explained as being due to a partial coating of the energizer with graphite.

Regeneration of Energized Compounds

The mechanism of the catalytic action exerted by certain carbonates in the carburization of steel has been the subject of much speculation and considerable experimental work. One of the most popular theories, to which, incidentally, the authors of this paper do not subscribe, claims that the acceleration in rate of carburization is due to the gradual decomposition of the carbonate, resulting in the formation of carbon dioxide, which reacts with the carbonaceous substance to produce carbon monoxide, a very active carburizing gas. Several exponents of this theory have claimed that after use such compounds will regain their activity if allowed to age under such conditions that the metallic oxide formed by the decomposition of the carbonate during carburization will have an opportunity to absorb carbon dioxide and thus revert to carbonate. Enos (11) apparently is the only investigator who has tried to test this question experimentally. In discussing the regeneration of compounds energized with barium carbonate Enos states, "Potter (Thesis, University of Cincinnati, 1930), was not able to bring about complete regeneration of the compound although numerous variations in procedure were tried".

In the present experiments, four carburizing compounds were used: (a) Plain hardwood charcoal, of the type previously described. (b) 90 per cent charcoal plus 10 per cent Na_2CO_3. (c) 90 per cent charcoal plus 10 per cent $BaCO_3$. (d) 90 per cent charcoal plus 10 per cent $CaCO_3$. In each instance, the charcoal was dried in a moisture oven before use. Each compound was tested for its ability to regenerate by the following experimental method.

Four retorts were packed with the same carburizing mixture. The assembly was heated for 7 hours at 950 degrees Cent. (1740 degrees Fahr.) and air-cooled. As soon as the retorts were cool enough to handle, which was a matter of some 15 minutes, the retorts were emptied, and the used compound was used to pack two retorts for a second carburizing test, which was run immediately, and which was exactly like the original one.

Four more retorts were packed with the same carburizing mixture and given the heat treatment outlined above. The four retorts were emptied, and the carburizing compound was exposed to the air for a matter of several months. At the completion of the air aging period, the aged compound was dried and was then used to pack two retorts for a final carburizing test which was exactly the same as the original one.

Four more retorts were packed with the same carburizing mixture and given the heat treatment outlined above. The four retorts were emptied, and the carburizing compound was treated with moist carbon dioxide gas till the energizer showed complete conversion into carbonate. This treated material was finally dried and then used to pack two retorts for a carburizing test which was exactly the same as the original one.

The air aged samples were left exposed to the air for 5 months. At the end of the aging period, chemical tests showed that the sodium was 99.2 per cent Na_2CO_3 and 0.8 per cent $NaHCO_3$. Hot water extracts gave well-defined positive tests for calcium and for barium, indicating that in those compounds the conversion into carbonate had not been completed.

The samples treated with carbon dioxide were subjected to a slow flow of the moist gas for approximately five months. From time to time samples were removed, extracted with hot water and the extracts tested to determine the completeness of conversion of the energizer into the carbonate form. The barium showed complete reversion to the carbonate quite readily, but the other energiz-

Table III
Average Data for the Regeneration of Mixtures

Weight Increase Grams Per Square Inch			Hypereutectoid Plus Eutectoid—Inches			Total Case Depth—Inches		
First Runs—Before Treatment								
			Sodium Carbonate Mixtures					
0.0593	0.0588	0.0579	0.0438	0.0424	0.0425	0.0744	0.0738	0.0733
			Barium Carbonate Mixtures					
0.0516	0.0525	0.0526	0.0419	0.0410	0.0406	0.0718	0.0733	0.0703
			Calcium Carbonate Mixtures					
0.0304	0.0309	0.0289	0.0176	0.0163	0.0136	0.0588	0.0576	0.0582
			Plain Charcoal					
0.0306	0.0313	0.0291	0.0179	0.0170	0.0163	0.0589	0.0572	0.0570
Second Runs—After Treatment								
Not Aged	Treated With CO_2	Air Aged	Not Aged	Treated With CO_2	Air Aged	Not Aged	Treated With CO_2	Air Aged
			Sodium Carbonate Mixtures					
0.0513	0.0507	0.0524	0.0415	0.0420	0.0420	0.0724	0.0722	0.0723
			Barium Carbonate Mixtures					
0.0485	0.0485	0.0498	0.0390	0.0390	0.0394	0.0710	0.0704	0.0708
			Calcium Carbonate Mixtures					
0.0221	0.0219	0.0189	0.0071	0.0068	0.0035	0.0523	0.0514	0.0491
			Plain Charcoal					
0.0213	0.0237	0.0218	0.0070	0.0075	0.0060	0.0490	0.0497	0.0496

ers took a surprisingly long time to go completely to the carbonate state. As a matter of fact, after four months, conversion was still incomplete, and a direct addition of steam was made to accelerate the rate of carbon dioxide absorption. At the end of the five-months' period, conversion of the calcium to carbonate form was complete. Tests on the sodium energized compound indicated that the sodium was present as carbonate and bicarbonate. The ratio of bicarbonate to carbonate varied considerably from point to point in the compound according to where the sample was taken from the carbonating apparatus. Prior to the final carburizing test, the compounds were all subjected to drying, and they were then mixed thoroughly.

The averages of the experimental data are given in Table III. The results are entirely negative. That is, the air aged samples, and the treated samples as well, showed no greater capacity to carburize than did the samples re-used immediately after the first run. The oft-stated idea that carbonate energized compounds will regenerate if carbon dioxide absorption occurs does not seem to be substantiated by experimental evidence.

Acknowledgment

The writers wish to express thanks for financial support received from the Wisconsin Alumni Research Foundation and from the research funds of the College of Engineering of the University of Wisconsin.

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DISCUSSION

Written Discussion: By John F. Wyzalek, chief metallurgist, Hyatt Bearings Division, General Motors Sales Corp., Harrison, N. J.

The authors present interesting test data which with the aid of practical interpretations should prove a valuable aid towards a better understanding of compound carburizing reactions.

Considering the frequent commercial use of calcium carbonate as an energizer, generally in conjunction with barium carbonate, it would be interesting to develop whether the authors' conclusion to the effect that calcium carbonate is an inert diluent is justified. Perhaps a series of tests with varying amounts of calcium carbonate added to a barium carbonate energized charcoal would prove of interest. Have the authors conducted any such tests?

The conclusion drawn in the paper that barium carbonate on second re-use seems to be entirely inert is certainly contrary to general belief and practical evidence considering the prevalent commercial practice of using indefinitely a compound consisting of 80 per cent and higher of used carburizer.

Without any intention to detract from the data presented, I wish to ask whether perhaps a somewhat different set of results would be derived if a similar test series was conducted with an attempt to more closely parallel actual practice? For instance, use of heat resistant alloy containers instead of

wrought iron pipe. Size and design of containers more approaching production usage. Also, carburizing temperature more in line in general practice, say, between 1675 and 1700 degrees Fahr. Undoubtedly other conditions in variance with commercial procedure may influence results which as presented by the authors may be confusing to those who in their actual production find indication not in line with their conclusions.

Written Discussion: By E. G. Mahin, professor of metallurgy and head, department of metallurgy, University of Notre Dame, Notre Dame, Ind.

The authors are to be commended for the careful investigation which is reported in this paper. At its best, commercial case carburization must be conducted along somewhat empirical lines and any effort which is designed to supply detailed information is of value.

Since it is generally recognized that the results obtained in commercial practice, on a large scale, do not necessarily parallel those observed in small-scale laboratory experiments, even when heating and time factors and nature of materials are identical, it is assumed that the authors regard their own results as comparative among themselves only. Even with this reservation, it seems unfortunate that such small carburizing containers were used and that the carburizers were employed in powdered form.

The normal course of carburizing reactions depends as definitely upon ready contact of reacting materials, as upon the heating cycle and the composition and physical state of the carburizer. Such contact involves free circulation of gases in the interstices of the granular carburizer and easy accessibility of the steel surface to the circulating gases. It is suggested that a powdered carburizer is not ideal in this respect; and a cylindrical steel specimen, $\frac{7}{16}$ inch in diameter, axially placed in a 1-inch pipe section, permits a layer of only $\frac{9}{32}$ inch of powdered carburizer (which could easily become more or less packed) around the sides. The force of this objection is, of course, lessened by the fact that the mid section of the steel cylinder is only 0.5 inch removed from the somewhat larger body of carburizer at the ends. The objection could have been entirely obviated by the use of larger carburizing boxes and of small granules, rather than powder, of carburizing compound.

With these points in mind, it would be of interest to know whether the carburized steel was sectioned for examination at more than one point on its axis and, if so, whether a case of uniform depth was found. Upon the basis of experience one could predict with reasonable assurance that the case would be deeper toward the ends of the piece.

The authors have noted a blackening of the steel specimens when barium carbonate or sodium carbonate was used as energizer and they have indicated that a deposit of graphite was formed. In some cases it was difficult or impossible to remove this deposit. Were any tests made to establish the identity of this material definitely as graphite? Ordinarily a graphite deposit is fairly light and easily removed. It seems possible that slight fusion of the energizing compound may have bound particles of the powdered carburizer to the steel surface and that this coating, naturally difficult of removal, might have been mistaken for graphite. Probably this point is unimportant but it raises the natural question as to the character of reactions responsible for possible graphite formation.

The authors have observed that the 2 or 3 per cent of moisture ordinarily present in the carburizer appears to exert no retarding influence upon the carburizing process, presumably when energizers are present in the carburizer. Possibly, as the authors state, the opposite view is due to certain theoretical considerations. In the earlier stages of the heating cycle, the evaporation of water and the thermal expansion of steam expel a certain amount of air from the carburizing pot. To this extent water vapor, instead of atmospheric oxygen, is left as the only oxidizing agent. The reaction of this with carbon, at higher temperatures, produces hydrogen and carbon monoxide in equal volumes. Hydrogen retards carburization, therefore undried and nonenergized charcoal should show reduced activity.

This retarding effect should be minimized by the presence of the energizer, which generates carbon dioxide (potential carbon monoxide), thus eliminating much of the water vapor by driving it from the carburizing vessel.

The authors reiterate their skepticism regarding the generally accepted theory concerning the mechanism of energizing reactions.[1]

There appears to be no evidence offered in this paper for this adverse view, other than the fact that regeneration of the energizer is not complete when the "spent" carburizer is exposed to air. This, it seems to me, is not very convincing evidence. As carbon is progressively oxidized at carburizing temperatures the inorganic compounds composing the ash must combine, to a certain extent, with the basic energizer. Partial fusion of the resulting slag-like material will certainly remove some of the energizer from the possibility of regeneration by combination with carbon dioxide.

On the other hand, exposure of the used carburizer to air, for regeneration of the energizer, is not by any means universal practice. If the explanation of energizer reactions which I have earlier suggested (loc. cit.) is correct, regeneration takes place automatically in the lower temperature ranges of the next succeeding carburizing operation. To whatever extent partial combination of energizer and ash has occurred, regeneration will be impossible by any means.

Oral Discussion

G. T. WILLIAMS:[2] In connection with this very fine paper I would like to bring up one question which might stimulate the authors to a little more work, although they probably have a long enough campaign already scheduled and are not interested in more suggestions.

I have frequently had the experience of seeing that work that was machined or ground on one side with scale on the other side will tend to carburize to a lower depth and lower maximum carbon on the machined side. That is particularly true in my observation when using a slow-burning type of compound.

Some brief experiments were undertaken to check this, and we found if we coated the machined side with iron oxide in the form of rust, or if we painted that surface with iron oxide, then the carburizing activity was equal

[1] E. G. Mahin's discussion following the papers by Grossmann and McQuaid, TRANSACTIONS, American Society for Metals, Vol. 26, 1938, p. 453.

[2] Metallurgist, Testing and Research Laboratories, Deere & Co., Moline, Ill.

on both sides. Barium carbonate also gave the same results if not put on too heavily; if it formed an impervious coating, it blocked rather than stimulated. One surprising thing we found: If we thoroughly moistened the compound by putting an eighth of an inch of water in the bottom of an ordinary carburizing box before running the carburizing tests, the machine side carburized to equal depth and density.

I am wondering whether the authors would like to speculate on the importance of iron oxide either in the compound itself or on the surface and the possible effect of water in that connection. It should be repeated that I am speaking of slow-burning, lower activity compound; the effect mentioned may be related to the lower carburizing potency of this type. It is possible that, with reduced available carbon, iron oxide strengthens or catalyzes its activity, while with plenty of available carbon, unoxidized surfaces also receive their share of carbon. In other words, perhaps the oxidized austenite faces take up carbon first, but if there is plenty this creates no difference.

H. H. LURIE:[3] The authors have done an excellent piece of work in determining the effects of the individual components in carbonate energizers.

Most commercial carburizing compounds have certain percentages of all three of the carbonates and we wonder if the authors have tried any combinations of these to learn what effects they produce as two or three component systems. The investigation of such a series would consume considerable time but the results would be very valuable as a check on the current practice in use in the manufacture of carburizing compounds. Previous investigators have often considered the sodium carbonate to be more active in the range of 1300 to 1400 degrees Fahr., the calcium to be active around 1500 to 1600 degrees Fahr., and the barium in the range of 1600 to 1700 degrees Fahr. Furthermore, it would seem logical, that if the calcium carbonate had practically no effect, as the authors have shown, that very few producers of carburizing compounds would add it to their products. We believe this is a case similar to metallic alloys where some elements are of little or no effect by themselves but when used in combination with one or more components, their complementary effect is almost unbelievable.

E. E. THUM:[4] I asked the chairman whether the meeting was open for some general remarks on the carburizing process and the aims to be sought. He was kind enough to say "Yes", and perhaps the general remarks I have to make on the trend of carburizing practice may be interesting and stimulating.

I think everyone will agree that carburizing in solid compounds is vastly better done today. We can all remember the hot, dirty and dusty hardening rooms which were "standard" 15 years ago. Today one would have little difficulty in finding carburizing operations, using solid compounds, done cleanly enough so it might almost be put into the machine line without creating a nuisance. So much for the housekeeping.

Carburizing, however, must stand scrutiny in the light of the general tendency to speed up production and cut down the time in process. Gas carburizing has been of help here, because there is no large mass of carbonaceous

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[3]Chief metallurgist, Cummins Engine Co., Columbus, Ind.

[4]Editor, *Metal Progress*, Cleveland.

solids which must be heated up before carburizing can begin. One of the prime reasons for the larger amount of gas carburizing being done is this matter of reduction in time required for the process (and by "gas carburizing" I include the carburizing in atmospheres produced by dripping a liquid into a hot container).

Unfortunately, the carburizing process is a diffusion process, and as such is something that really does require time for the necessary transport of carbon from the surface of the steel inward. The only way to reduce the times of the chemical and physical reactions is to increase the factors such as temperature and gas concentration which will increase the rate of diffusion. Since there are commercial limitations on both temperature and concentration, undoubtedly the easiest way to reduce the time is to reduce the amount of extraneous material which must be heated. The use of the proper combination of energizers, as studied by Messrs. Sutton and Ragatz, is also a factor in speeding up the carburizing process.

Another factor leading in the same direction is the pretty general realization by metallurgists that a great deal of carburization has been done in the past that is really unnecessary. If the part itself is studied it will frequently be found that it is entirely unnecessary to make as deep a case as is done conventionally. The trend unquestionably is toward shallower and shallower cases. It is not hard to find parts now produced in vast numbers where the cases can be measured in thousandths rather than eighths of an inch.

You can figure for yourself what a reduction of time would be possible by a reduction in the depth of case to that really required in service. Quite obviously, if the pressures between contacting parts are low and intermittent and the lubrication proper, a hard surface of almost microscopic thinness could be maintained by proper support which would serve just as well as a case which is very much thicker.

There is always the tendency, of course, to use the higher carbon materials, and surface harden them by any one of two or three recently developed processes. Those methods are very widely used indeed and are cutting in on the use of solid carburizers.

Reverting again to the matter of gas carburizing in very rapid time, I recently observed at the National Cash Register Co. the carburization and hardening of teeth on a small rack by one passage of small oxyacetylene flames, adjusted to have an excess of acetylene. The production rate was about 350 a day. The rack was stamped from cold-rolled, low carbon sheet steel. The flame was on each tooth a matter of seconds; the resultant case, of course, was very thin but nevertheless it was really file hard. There was enough strong material backing up that hard surface so you had to work on those teeth a long while with a testing file before you could break through and get the file to bite.

A good deal of carburized work is assembled in a brazing furnace. The question of decarburization comes up there, and I believe it may be news to a good many of you that in all probability the moisture in prepared gas is the bad actor. If almost any prepared gas is dried with activated aluminum, that is, dried really *dry*, you can bring the material out of a brazing furnace without measurable surface decarburization.

Speeding a production schedule may mean changes all along the line. Often the matter of volume change is of as much importance as the proper surface. We therefore find a decided tendency toward lower temperature heat treatment, where change in volume and shape is to be held at the lowest possible amount. This is the reason for the growing use of nitriding the special alloy steels, as well as surface hardening in mixtures of carbon, cyanogen and nitrogen-bearing gases, which is successfully done at low temperature on ordinary steels.

Authors' Reply

Mr. Williams, in the oral discussion, cites some of his results which indicate that a layer of iron oxide on the surface of the steel accelerates the rate of carburization, and he asks whether the present authors have any comment to offer on this result. While we have not performed any tests on the influence of iron oxide coatings, we wish to call attention to the results obtained in an earlier investigation[5] which showed that iron oxide, when mixed with hardwood charcoal, exerts a definite energizing action. Furthermore, Guthrie,[6] who did some of the early work on gas carburization, demonstrated that a thin film of iron oxide which was allowed to form on the surface of the steel prior to the initiation of carburization would accelerate the rate of carbon absorption. In each of the two instances cited the iron oxide undergoes reduction to the metallic state, and the finely divided iron thus produced appears to accelerate the carburizing reactions.

Both Messrs. Mahin and Wyzalek express some concern over the fact that the equipment and the experimental methods did not approach commercial conditions more closely. The present authors gave considerable attention to the problem of adopting equipment and experimental procedures which were capable of giving accurate and reproducible results. They were fully aware when they embarked upon their experimental program that their equipment and certain details of procedure did not duplicate commercial conditions. However, it was felt that the principles of carburization could be studied best by using small-scale laboratory equipment, as is usually done in the investigation of other chemical reactions. The authors are very definitely of the opinion that experimental work on the principles of carburization has in too many instances been carried out in equipment of such large scale that the results were difficult to interpret, and incorrect conclusions resulted. Consider, for example, the use of the small retorts used by the present authors as compared to the use of large sized commercial boxes. The use of the small diameter retorts permitted rapid heating, and the thermal conductivity of the compound was of little importance. Lag tests showed that the center of the retort arrived at the desired carburizing temperature only a few minutes after the thermocouple in the furnace muffle indicated that the carburizing temperature had been achieved. All of the steel specimens were similarly located in the retorts, and excellent duplication of results was obtained. In using carburizing boxes of commercial size, heating rates are relatively slow, and a fairly long time is

[5]Reference 9 in the Bibliography.

[6]R. G. Guthrie and O. Wozasek, "Gas Carburization of Steel", TRANSACTIONS, American Society for Steel Treating, Vol. 12, 1927, p. 853.

required for the heat to penetrate to the interior of the retort. The degree of carburization is affected to some degree by the location of the specimen in the box.

The authors wish to discuss quite fully the contention that a powdered compound will not carburize as satisfactorily as a granular compound, all other factors being the same. From theoretical considerations, we should expect a powdered carburizing compound to show a faster rate of carburization than a granular compound under like conditions. This deduction may be arrived at through the following line of thought. When the steel is undergoing carburization, two surface reactions are occurring simultaneously. At the surface of the steel,

$$3\ Fe + 2\ CO \rightarrow Fe_3C + CO_2$$

At the surfaces of the adjacent carbon granules,

$$C + CO_2 \rightarrow 2\ CO$$

Concentration differences with respect to carbon dioxide and with respect to carbon monoxide are developed betweeen the steel–gas interface on the one hand and the carbon–gas interface on the other hand. A continual transfer of carbon monoxide from the carbon to the steel and a continual transfer of carbon dioxide from the steel to the carbon occur throughout the carburizing operation. This continual flow of gas is a diffusional process following Fick's diffusion law, and should not be confused with thermal convection which occurs only when temperature inequalities exist. The diffusion law is expressed by the following equation:

$$\begin{aligned} dW/d\theta &= kA\ (dc/dx) \\ dW/d\theta &= \text{rate of material transfer} \\ k &= \text{diffusion constant} \\ A &= \text{area} \\ dc/dx &= \text{concentration gradient} \end{aligned}$$

It is apparent from an inspection of this equation that if the concentration gradient dc/dx is increased, the rate of material transfer between steel and carbon will be increased, all other factors being equal. Since the gas compositions established at the steel–gas interface and the carbon–gas interface are probably those corresponding to equilibrium conditions, the overall concentration differences between the two surfaces where the reactions are occurring will be fixed at definite values determined by the temperature of the system and the carbon content of the austenite comprising the outer layer of the steel. If we decrease the mean effective distance between the steel and the carbon granules by diminishing the particle size, the concentration gradient dc/dx will rise, and the rate of material transfer between the carbon and the steel should be increased. Several years ago, Messrs. R. L. Beyerstedt and H. L. Lautz, two senior students working under the direction of one of the present authors, obtained some experimental data which verified the foregoing deduction which was made on theoretical grounds. This was done in two ways. In the first set of tests, a lot of hardwood charcoal was crushed and screened to various sizes, and carburizing tests were run on these various sizes of charcoal. It was found that the smaller the particle size, the faster the rate of carburization. The results are summarized as follows:

Charcoal Size		Weight Increase Grams
Through Screen	On Screen	Per Square Inch
No. 3	No. 4	0.0154
4	6	0.0175
6	10	0.0181
10	20	0.0186
20	35	0.0193
35	..	0.0226
Powdered	..	0.0236

Carburizing Material: Hardwood charcoal; no energizer added.
Carburizing Treatment: 6 hours at 1750 degrees Fahr. (950 degrees Cent.); retorts air-cooled.

In the second set of experiments, two widely used commercial carburizing compounds were employed. With each material, tests were run employing the material in the granular as-received state, and also in the finely powdered condition. With both materials, the finely powdered state gave the faster rate of carburization, as is indicated by the following summary of results.

	Weight Increases, Grams Per Square Inch	
	As Received; Granular	Powdered
Commercial Compound A.....	0.0448	0.0469
Commercial Compound B.....	0.0349	0.0434

Carburizing Treatment: 6 hours at 1750 degrees Fahr. (950 degrees Cent.); retorts air-cooled.

While there would be many objections to using a powdered carburizing agent in production work, the authors feel that the above results demonstrate conclusively that the use of fine material will accelerate rather than retard carburization. It is felt that the use of finely powdered carburizing compounds in the present investigation aided in the production of reproducible results, and in the production of specimens that showed excellent uniformity of carburization at all points.

Professor Mahin raises a question regarding the identification of the black deposit that was observed in many instances, and which has been designated as graphite by the present authors. Identification of the deposit as graphite was made on the basis of the black shiny appearance when the surface was rubbed, its slippery feeling and its insolubility in hot water.

The authors are familiar with Professor Mahin's explanation of the mechanism of energizer action, as presented in a discussion contributed to the Carburizing Symposium held by this Society in 1938.[7] This theory is an amplification of the familiar carbon dioxide evolution theory of energizer action. Professor Mahin adheres to the theory that the accelerating effect produced by sodium and barium carbonates is due to the gradual decomposition of the carbonate, which produces an enrichment of the gaseous atmosphere with respect to carbon monoxide because of the interaction between the released carbon dioxide and the hot carbon present in the retort. The unique feature of the theory as presented by Professor Mahin is that he holds that all used compounds are automatically regenerated on reheating to the carburizing temperature, through the combination of the carbon dioxide in the retort with any oxide that may be present in the compound. This theory was offered to explain the experimental

[7]E. G. Mahin, in discussion following papers by Grossmann and McQuaid, TRANSACTIONS, American Society for Metals, Vol. 26, 1938, p. 453.

fact that a compound energized with an oxide or with a hydroxide exhibits exactly the same degree of activity as a compound energized with an equivalent amount of the corresponding carbonate.

The present authors agree with Professor Mahin's contention that the results of the regeneration tests which are summarized in Table III do not disprove his theory. If, as Professor Mahin postulates, automatic re-formation of the carbonate is obtained on heating, then absorption or lack of absorption of carbon dioxide on aging at room temperature should produce no detectable result. The results presented in Table III merely prove that the oft repeated statement that used compounds increase in activity on aging seems to be without foundation of fact.

The only evidence cited in the present paper which is not in accord with the theory that the catalytic effect of soduim carbonate is due to a gradual evolution of carbon dioxide is to be found in the paragraph on page 194, wherein the decomposition of the carbonate in use is briefly discussed. It is there pointed out that the extraction tests on certain of the compounds energized with sodium carbonate showed that the extracted alkali was practically all in hydroxide form, which would indicate practically complete decomposition of the carbonate. Yet there is no evidence that the catalytic activity was lessened by the almost complete decomposition of the carbonate.

In conclusion, the authors wish to express their sincere appreciation of the discussion which has been presented. The gentlemen who have so kindly offered their comments are men who have made many valuable contributions to the literature on carburization, and their comments accordingly are of interest and value to the authors.

RECOVERY OF NICKEL FROM COLD WORKING ON ANNEALING

By Erich Fetz

Abstract

The contributions in this paper aim at two objects: first, to place, in general, the experimental technique of recovery tests of cold-worked metals on a more and more rational and scientific basis, and second, in particular, to study further factors which may be responsible for the unusually wide temperature range of softening of cold-worked nickel as established by different investigators.

This paper concerns itself mainly (a) with the stress distribution and the uniformity of the relief of working strains throughout the test specimen, particularly at small plastic deformations, and (b) with the effect of thermal pretreatment at 500, 900 and 1300 degrees Cent. and of grain size on the characteristics of recovery from cold working on annealing. The effect of these factors was studied by means of hardness measurements using carbonyl nickel powder metal and electrolytic nickel as testing materials.

Introduction

In previous studies (1-5)[1] the effect of the following factors on the recovery of nickel from cold working on annealing was investigated: chemical composition, amount of plastic deformation, annealing time, deformation speed, furnace atmosphere, thickness before rolling, and origin of testing material (powder metal versus solidified and electrodeposited nickel). Comparatively speaking, only the purity of the testing material was found to exert a very pronounced, though varying effect upon the location of the recovery* temperature range. This influence of contaminations was established as the main reason why, for instance, recrystallization of cold-worked, melted nickel was found as low as 350 degrees Cent. (3) and as high as over 1100

[1]The figures appearing in parentheses refer to the bibliography appended to this paper.

*As a characteristic value of the "recovery", that temperature T_r is used, at which 50 per cent of the hardness gain due to cold working or other change of physical properties is lost during a 30-minute anneal.

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degrees Cent. (6). The effect of only magnesium, iron, manganese (7), silicon, tin and copper (4) on the recovery of tensile strength and hardness of nickel has been systematically investigated. Owing to the drastic effect of residual amounts of the deoxidizers, in particular of the widely used magnesium, the powder metallurgical approach to this problem has been advocated (4). The phenomenally low hardness recovery and recrystallization temperature ranges found by the author (2), (3), (4), (5) on nickel made from compressed carbonyl powder, has been recently confirmed abroad by X-ray and tensile tests (8).

The effect of the amount of plastic deformation is rather puzzling and apparently of the second greatest importance. In one case, every change of 10 per cent reduction in rolling, shifts the softening temperature by only 12.1 degrees Cent. (melted carbonyl powder nickel) while in another the shift amounted to 31 degrees Cent. (compressed, wrought, 3 times recrystallized, vacuum-annealed carbonyl powder metal).

As will be shown below, a maximum shift of 38.4 degrees Cent. per 10 per cent reduction was obtained on electrolytic nickel, annealed at over 1300 degrees Cent. (2370 degrees Fahr.) prior to plastic deformation. The 90 per cent cold-rolled sample recovered at 352 degrees Cent., while 10 per cent cold-rolled material loses half of its work hardness at 659 degrees Cent. (1220 degrees Fahr.). The melted carbonyl nickel softening in the narrowest temperature range found with nickel, recovers at 389 and 486 degrees Cent. (730 and 910 degrees Fahr.) respectively from a 90 and 10 per cent reduction. In one case the softening range extends 307 degrees Cent. (585 degrees Fahr.), and in the other only 97 degrees Cent. (180 degrees Fahr.) for the same plastic deformation.

This greatly varying behavior makes it mandatory to determine the entire softening temperature range for each material tested. Most of the 24 former investigators determined the recovery of nickel from only one degree of plastic deformation, in each case. Comparisons between their findings can hardly be made, as some experimenters applied a deformation of only 10 per cent, others one of over 90 per cent.

In all previous 17 cases studied (2), (3), (4) a straight line relationship between percentage reduction in cold rolling and recovery temperature was established. This law has been confirmed in the 10 cases reported in this paper. The cause of the greatly varying slope

of the T_r per cent reduction curve had not been discovered, and thus called for further experiments as this factor evidently has a great bearing on the characteristics of recovery from cold working.

In comparison with the pronounced effect of purity, amount of plastic deformation, and, perhaps, time of annealing, the other factors such as speed of plastic deformation, furnace atmosphere, and thickness before rolling exert a relatively small, if any, influence on the recovery characteristics. Regarding the origin of the testing material and its previous history, further experiments appeared to be necessary.

Effect of Stress Distribution

Problem: In some former hardness recovery tests, particularly at small plastic deformations, the upper and lower side of a test specimen did not furnish identical softening curves. They also were not identical in some cases when obtained from the same side but at different hardness testing loads. The only difference appeared to be the depth of penetration of the indenting tool. Even hardness readings on the same plane were found to vary at small reductions, while hardly any differences occurred at severe plastic deformations.

This evidence seemed to indicate a nonuniform stress distribution in the surface layers at small reductions at one hand and differences in the penetration of the induced cold working strains at the other. If that be the case and more latent energy is stored at the surface of some test pieces than in others, a lower recovery temperature of the sample more severely deformed at the surface and, in consequence, a different inclination of the T_r/per cent reduction curve would result.

It appeared desirable to study this possible variable affecting the characteristics of hardness recovery. Only deformations of at least 25 per cent were applied in the former recovery tests (2-4). Since the above described variations seemed to be more pronounced the smaller the reductions, a relatively mild plastic deformation of about 10 per cent was included in these tests.

Materials and Methods: Electrolytic nickel, Grade A, (a) in the electrodeposited state and (b) in the wrought and annealed state was used. The object was to compare fine grain material (a) with a coarse grain (b) of presumably the same chemical analysis.

The distribution of the strain hardening induced by 10 and 25 per cent cold rolling and the recovery therefrom was determined with

the Rockwell superficial hardness tester. All readings are converted into Brinell numbers using the latest conversion chart No. 38 issued for the Rockwell machine.

The pretreatment of (a) was as follows: The uneven surfaces of the electrodeposited nickel were removed on a milling machine and the marks from milling on a belt grinder. In order to produce a small grain size the sample was then annealed at 650 degrees Cent. for 1 hour with 1 hour for heating and cooling. The mean hardness after annealing was RS-30T = 26.5 or 60 Brinell. The sample of 0.154 inch thickness was then rolled 10 per cent, cut in half and the rest rolled 25.9 per cent.

Specimen (b) of the same origin having a thickness of 0.265 inch was annealed, cold rolled 11.1 per cent (hardness as rolled = 73 RS-30T or 162 Brinell), slowly heated in hydrogen in 2½ hours to 1000 degrees Cent. and rapidly cooled in the furnace. Another reduction in cold rolling of 36 per cent (Brinell hardness = 169) was then applied followed by slow heating in hydrogen to 1000 degrees Cent. in 2½ hours. The upper and lower side had practically the same hardness of 7 RS-30T, which falls outside of the range of the conversion table. The Brinell hardness is thus lower than 53.

This series of mechanical and thermal treatments is considered to have obliterated, if not abolished, the structural effect of the electrolytic origin of the nickel. The sample was finally cold-rolled 10.8 and 25.3 per cent.

The difference in grain size is shown in Figs. 1 and 2. The samples were etched in 50 per cent aqua regia. According to the A.S.T.M. scale (9) the mean number of grains per square inch would be 2 and 64 respectively for the coarse and fine grain sample. Although sample (a) lost its electrodeposition hardness, no substantial grain growth took place. Nickel loses its electrodeposition hardness between 400 and 600 degrees Cent. (750 and 1110 degrees Fahr.). Slight structural changes take place at 550 to 650 degrees Cent. (1020 to 1200 degrees Fahr.), while coarsening of grain occurs at 850 to 1100 degrees Cent. (1560 to 2010 degrees Fahr.) (10), (11). Grain growth, which is absent at 1100 degrees Cent. (2010 degrees Fahr.) in the hardest electrodeposits also depends on hardness and original structure (12), (13).

In order to prove the penetration of the cold rolling effect, the hardness and its recovery was tested at the surface A, on an intermediate plane B 0.02 and 0.015 inches below the surface of the 10

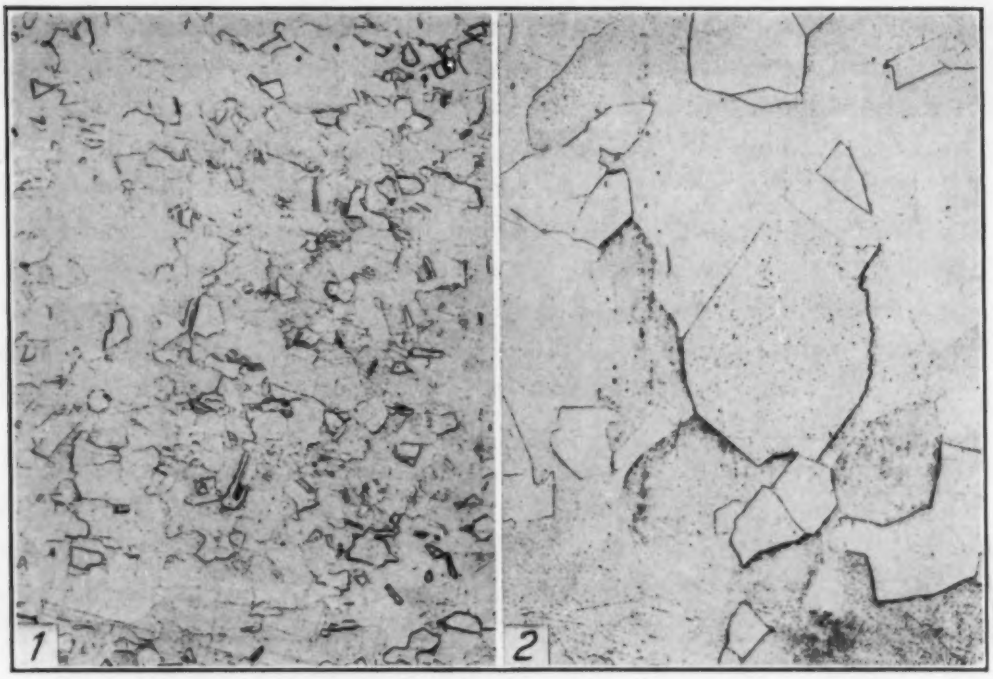

Fig. 1—Small Grain Electrolytic Nickel Annealed at 650 Degrees Cent. (1200 Degrees Fahr.). × 100.
Fig. 2—Large Grain Electrolytic Nickel Twice Cold-Rolled and Recrystallized at 1000 Degrees Cent. (1830 Degrees Fahr.). × 100.

and 25 per cent rolled samples respectively, and in the central region C 0.04 and 0.03 inches underneath the surface. Incidentally, the depth of indentation of the Rockwell superficial hardness tester is less than four thousandths of an inch. The inserts in Figs. 3 to 6 show schematically how the samples were prepared in the milling machine.

Results: The hardness distribution throughout the samples and the hardness variations on the same plane are given in Tables I, II and III. The mean hardnesses tabulated represent 3 (all identical) or more readings. Variations from 0 to 20 Brinell units apparently occur on the same surface. (Table I and II). The hardness variations along the surface are more pronounced in the 25 per cent cold-worked sample of the fine grain electrolytic specimens (a) than in the 10 per cent cold-rolled metal. The conditions are reversed for the samples of group (b), i.e., greater variations in hardness occur in the samples which have been cold-worked least.

Regarding the hardness variations in relation to depth (Table III) we find a considerably greater hardness at the surface of the fine-grained nickel samples cold-rolled 10 and 25 per cent. A loss of 7.5 Brinell (10 per cent reduction) and 9.5 Brinell (25 per cent reduction) takes place respectively 0.02 and 0.015 inches below the

Table I

Material				Fine grain Electrolytic Ni		Coarse grain Electrolytic Ni Annealed, rolled 11 Per Cent, annealed, rolled 30 Per Cent, annealed in 2 hrs. to 1000 Degrees Cent.	
Pretreatment				Annealed 1 hr. at 650 Degrees Cent.			
Brinell Hardness as converted from Rockwell Superficial ST-30				162		< 57	
Amount of Cold Rolling				10 Per Cent	25.9 Per Cent	10.8 Per Cent	25.3 Per Cent
Brinell Hardness	A) Surface	Upper Side	Mean	144	172	133½	162
			Max.	150	180	137	169
			Min.	140	169	127	160½
		Under Side	Mean	147	180	128½	159
			Max.	150	187½	128½	159
			Min.	144	172	128½	159
	B) Intermediate Layer	Upper Side	Mean	137	162	135	164
			Max.	139	165	137	169
			Min.	135	160½	130	162
		Under Side	Mean	139	171	132	159
			Max.	143½	172	137	162
			Min.	136	169	127	153
	C) Central Region	Upper Side	Mean	136½	165	122	160
			Max.	141	176	127	160½
			Min.	136	156	118	156
		Under Side	Mean	137	172	120	159
			Max.	141	176	127	160½
			Min.	136	169	117	156

Table II
Maximum Hardness Deviations in the Direction of Rolling

Material			Fine grain electrolytic nickel		Coarse grain electrolytic nickel	
Amount of Cold Rolling			10 Per Cent	25.9 Per Cent	10.8 Per Cent	25.3 Per Cent
Brinell Hardness Difference	(A) Surface	Upper Side	9	11	10	9
		Under Side	6	15½	0	0
	(B) Intermediate Layer	Upper Side	4	4½	10	9
		Under Side	7½	3	7	7
	(C) Central Region	Upper Side	3	20	9	6½
		Under Side	5	5	10	4½

Table III
Hardness Variations with Depth

Material			Fine grain electrolytic nickel		Coarse grain electrolytic nickel	
Amount of Cold Rolling			10 Per Cent	25.9 Per Cent	10.8 Per Cent	25.3 Per Cent
Brinell Hardness	Surface → Intermediate Layer	Upper Side	−7	−10	+1½	+2
		Under Side	−8	−9	+3½	±0
	Intermediate Layer → Center	Upper Side	−½	+3	−13	−4
		Under Side	−2	+1	−12	±0

surface. Contrary to this behavior, a slight increase of hardness with depth of 2.5 Brinell (10 per cent reduction) and 1 Brinell (25 per cent reduction) is noticed in the coarse grain wrought nickel. Within

the error of reading, hardness variations in depth were practically absent in only one case, namely in the 25 per cent cold-rolled coarse crystalline wrought nickel (b). However, the hardness difference between the surface and central region of the 10 per cent cold-worked sample is notable (12.5 Brinell softer in the center).

It may be said in summary that the hardness tests revealed uneven work-hardening in both directions, e. g., on planes in the direc-

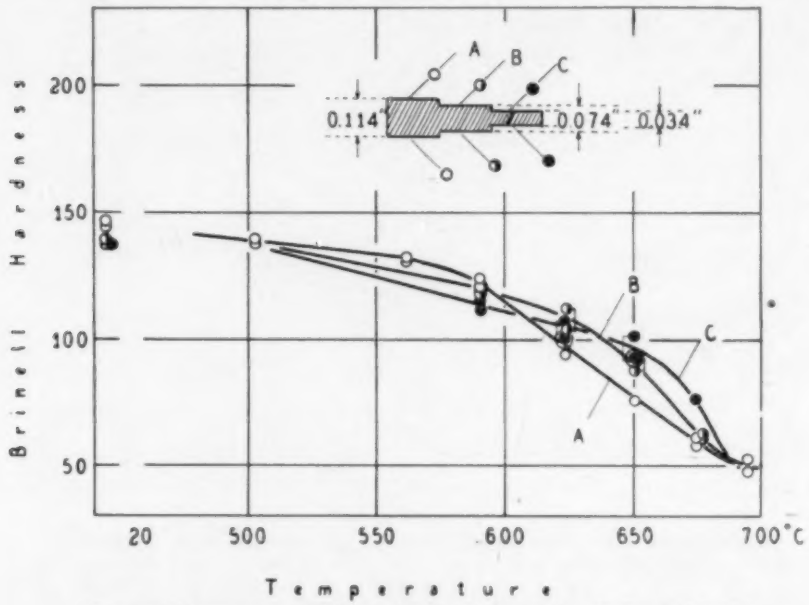

Fig. 3—Recovery at Different Depths of Fine Grain Nickel from 10 Per Cent Reduction.

tion of rolling and perpendicular to them with depth. The question arises whether these variations are also manifest in the recovery characteristics.

Individual samples of (a) and (b) were annealed for 30 minutes at different temperatures and then tested for hardness. The softening curves representing the mean hardness of both upper and lower sur-

Table IV
Recovery Temperatures T_r

Material	Fine grain electrolytic nickel		Coarse grain electrolytic nickel	
Amount of Cold Rolling	10 Per Cent	25.9 Per Cent	10.8 Per Cent	25.3 Per Cent
°C. (A) Surface	624°	587°	602°	560°
(B) Intermediate Layer	646°	590°	655°	593°
(C) Center	658°	593°	630°	572°
Difference: Surface → Intermediate Layer	+22°	+3°	+53°	+33°
Difference: Intermediate Layer → Center	+12°	+3°	−25°	−21°

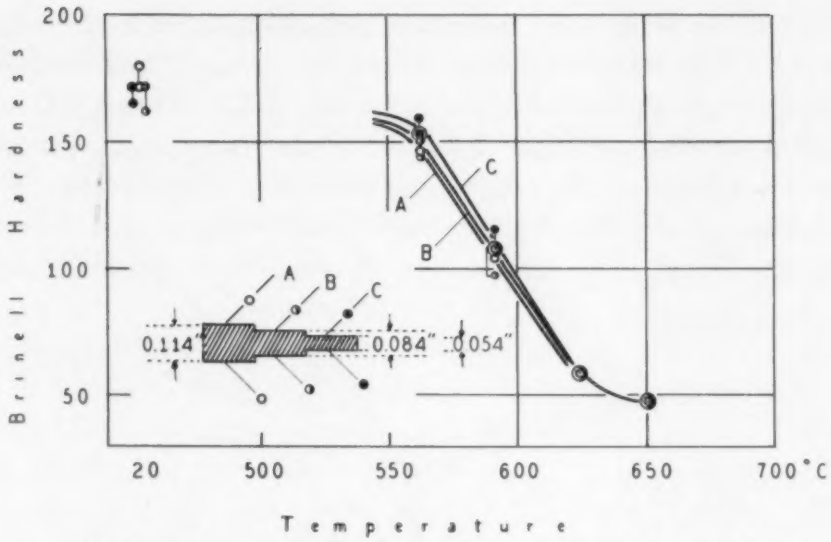

Fig. 4—Recovery at Different Depths of Fine Grain Nickel from 25.9 Per Cent Reduction.

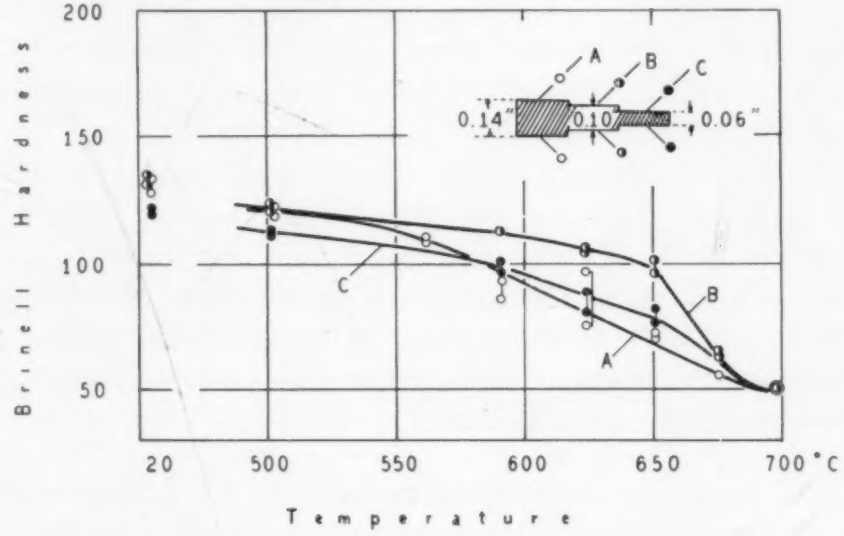

Fig. 5—Recovery at Different Depths of Coarse Grain Nickel from 10.8 Per Cent Reduction.

faces are shown in Figs. 3 to 6. The open, half black, and black circles respectively refer to the mean hardness on (A) the surface, (B) intermediate, and (C) central planes.

The recovery values T_r are given in Table IV. In the fine grain sample cold-rolled 10 per cent, (Fig. 3) the surface softens at a markedly lower temperature than regions at a depth of 0.02 inch, which in turn loses half of its work hardness at a lower temperature than the central region. This would indicate that more cold work energy has been stored at the surface. The cold rolling seems to

have uniformly penetrated the entire fine grain metal at 25.9 per cent reduction. The recovery temperatures of surface, intermediate and central region are practically the same, i.e. 587, 590 and 593 degrees Cent. respectively (1090, 1095 and 1100 degrees Fahr.) (Fig. 4).

In the coarse grain samples cold-rolled 10.8 per cent (Fig. 5) and 25.3 per cent (Fig. 6) the surface recovers at the lowest tem-

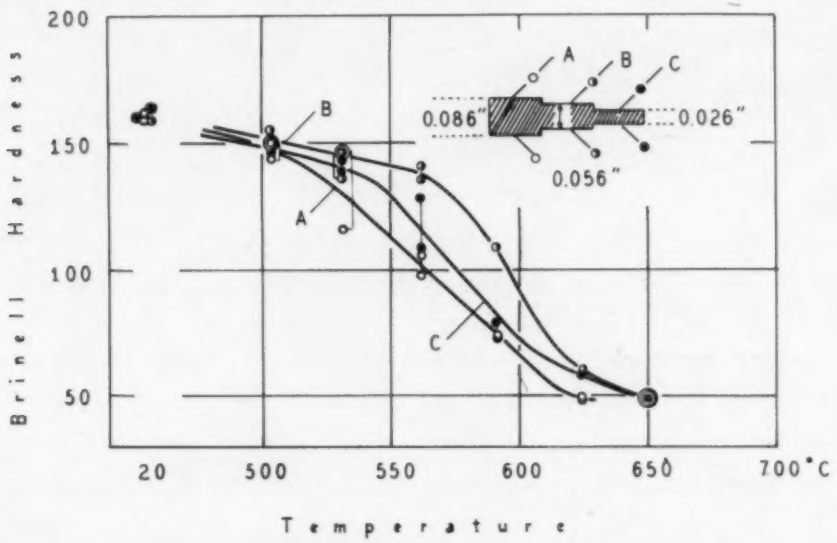

Fig. 6—Recovery at Different Depths of Coarse Grain Nickel from 25.3 Per Cent Reduction.

perature in both cases, followed by the central parts. It is surprising that the intermediate layers soften in a notably higher recovery temperature range than center and surface. The initial hardnesses furnish no clue for this phenomenon.

Discussion

On the whole there seems to be no simple correlation between work hardening and hardness recovery on annealing. The hardness test thus appears to be no quantitative indication of the inner state of the cold-worked metal and of the amount of stored energy. It was also previously found that the greatest strain hardening effect takes place in carbonyl nickel containing 0.25 per cent tin. Yet this material, recovers at a temperature almost 300 degrees Cent. (570 degrees Fahr.) higher than that of equally severely wrought carbonyl nickel powder samples although the latter shows considerably smaller strain hardening effects (4).

The uneven distribution of stresses in plastically deformed metal-

lic materials has been the subject of numerous studies. Unequal grain size after recrystallization of mildly deformed aluminum-magnesium alloys (14) and in Armco iron (15) has been directly attributed to uneven stress distribution in rolling. It has also been demonstrated by X-rays (16) that at any moment during recrystallization aluminum-copper alloys plastically deformed up to 20 per cent consist of completely recrystallized regions and all kinds of transitions of the disturbed lattice. Hardness tests over the cross section of cold drawn brass revealed very considerable differences in the penetration of strain hardening (17). Up to about 15-20 per cent reduction, the surface of cold-rolled copper bars hardens more than material at the middle of the side (18). Recrystallization of lightly rolled lead (19) commences at the edge of the slabs and proceeds inwards, because the surface layers are distorted considerably more than the center of the metal in the early stages of rolling. In pressing, the surface hardening effect is by far less pronounced.

Uniformity of rolling deformation increases as the thickness of the specimens decreases (19). In test pieces of the thickness as employed in these recovery tests a more uniform stress distribution was expected. It thus appears that the method of plastic deformation and the dimensions of the test piece do affect the characteristics of the recovery from cold work hardening on annealing. Inasmuch as there seems to be no direct correlation between the indentation hardness, amount of stored latent energy and recovery temperature, a considerable complication of scientific determination of the recovery ensues since the internal state of the testing material can hardly be adequately characterized.

This complication becomes the more confusing as conditions change from spot to spot within the same test piece at small reductions. The markedly different fashion in which, for instance, the surface layers and central regions of the 10 per cent cold-rolled, fine grain nickel (Fig. 3) recovers from cold working illustrates this point. It becomes obvious that the course of the softening curve depends on the depth of the penetration of the hardness tester and on the dimensions of the indenting tool. The conclusion appears justified that recovery curves as obtained by tensile tests may furnish results different from hardness determinations as the former represent the summary behavior of the entire cross section, while hardness tests represent only local conditions. The uneven recovery throughout the test piece has also been noticed in magnetic tests of

the recovery of twisted nickel wires. Portions of the testing material may have completely recovered while others are still in the hard state (20).

Going from surface to center, the recovery temperatures are progressively raised in the fine grain material. Why the intermediate region in the coarse grain nickel recovers in a notably higher temperature range is difficult to interpret. Lattice disturbances at the outside of single and multicrystalline tungsten wires were greater than directly underneath the surface. Towards the center, the lattice disturbance increased again (21). In compressed cylinders of mild steel, the Brinell hardness was greatest in the layer midway between the top and bottom surface (22).

A difference of 53 degrees Cent. was found between the recovery temperature of the surface and at 0.02 inches below the surface of coarse grain nickel (Fig. 5). With a heavier load and larger penetrator than used with the Rockwell superficial hardness tester a different T_r value would obviously be obtained on the surface. These observations furnish an explanation why the greatest deviations from the straight line T_r/per cent reduction relation was usually found in the case of mild plastic deformations.

It may be concluded that these variations in the distribution of cold working effects and relief on annealing accentuated by the testing method must be taken into account in scientific tests on recovery from cold working.

Effect of Preannealing

Comparing Figs. 3 and 5 and Fig. 4 with Fig. 6, notable differences in the recovery behavior of both materials derived from the same source are apparent. The principal difference deliberately aimed at is the grain size. Since the grain size is a function of the annealing temperature, a thorough study of this effect on hardness recovery of nickel appeared to be important.

Koref (23) found that single crystals of tungsten cold drawn 81 per cent did not soften when heated for 10 minutes to 1800 degrees Cent. (3270 degrees Fahr.) while fine grain material begins to soften when heated for 1 minute to slightly above 700 degrees Cent. (1290 degrees Fahr.). The amount of plastic deformation is not given, and it is also not stated whether both materials have the same chemical analysis. Angus and Summer (24) found that cold-worked copper having a grain size of 2 grains per square millimeter softens

at 500 degrees Cent. (930 degrees Fahr.) (beginning of recrystallization at 400 degrees Cent.) while fine grain copper of 1300 grains per square millimeter softens at about 250 degrees Cent. (no recrystallization noticeable at 400 degrees Cent.). However, these experiments are practically invalidated since

(a) the testing materials were not identical; arsenical copper (0.07 per cent arsenic) being compared with electrolytic copper;

(b) the amount of reduction was not the same in all tests.

The experimenters actually failed to find a pronounced effect of grain size on work hardness and softening temperature with cold-worked bronze. In view of this contradicting evidence, the effect of annealing (grain size) on the recovery is reinvestigated.

Materials and Methods: The following three kinds of nickel were used

(I) Carbonyl nickel made from powder without melting

(II) Electrolytic nickel, grade A, as deposited and

(III) Electrolytic nickel, grade A, cold-rolled and recrystallized.

The history of the materials tested is as follows: (I) The carbonyl powder (I.G. Farbenindustrie) of less than 325 mesh was hydraulically compressed at 50 tons per square inch in a tool steel die of 1 inch inside diameter. The compressed powder slug was heated slowly in 1¼ hours to 700 degrees Cent. (1290 degrees Fahr.) in a horizontal quartz tube furnace in flowing hydrogen and was furnace cooled in 30 minutes. Sintering was continued in a vertical quartz tube placed into a coil of a high frequency induction furnace by holding the sample for 5 minutes at about 800 degrees Cent. (1470 degrees Fahr.), 3 minutes at about 1200 degrees Cent. (2190 degrees Fahr.) and 2 minutes at over 1400 degrees Cent. (2550 degrees Fahr.). The hydrogen was pumped off and replaced 3 times. The sample rested on a carbonyl nickel slug to avoid contamination. The cylindrical specimen was then machined to an 0.707 x 0.707 inch square piece and cautiously reduced 26 per cent of its cross sectional area in a small experimental mill. (2 high, $3\frac{7}{16}$ inches diameter rolls, 12 revolutions per minute). The sample was then hydrogen-annealed at about 1200 degrees Cent. (2190 degrees Fahr.) for a few minutes by induction heat. Another reduction of cross sectional area of 35.6 per cent was applied, followed by a 1-hour hydrogen-anneal at 850 degrees Cent. (1560 degrees Fahr.) in a horizontal furnace (1 hour heating-up time). A third plastic deformation, this

Table V

Sample No.	Material	Annealing Treatment Temperature Degrees Cent.	Time	Hardness after Annealing Brinell	Initial Thickness before Cold Rolling in Inches	Work Hardness After Cold Rolling in Brinell Per Cent 30	Per Cent 60	Per Cent 90	Recovery Temperatures of Samples Cold-Rolled Per Cent 90	Per Cent 60	Per Cent 30	Total Extension of Recovery Temp. Range for 30-90 Per Cent Reduction in Degrees Cent.	Shift of Recovery Temp. by every 10 Per Cent Reduction Degrees Cent. 10 Per Cent
1	Carbonyl	500	5 hrs.	96	0.175	215	242	257	413	455	507	94	15.7
2	Powder Metal	900	1 hr.	78	0.175	199	234	253	423	466	527	104	17.33
3		1300 —1450	3 min.	64	0.175	189	231*	244	450	516	582	132	22.0
..	Grade "A"	as deposited		[208]	0.224	232	244	252	262	285	312	50	8.33
4	Electrolytic	500	5 hrs.	117	0.224	206	223	237	291	338	389	98	16.33
5	Nickel as	900	1 hr.	<57	0.224	174	208	226	344	440	520	176	29.4
	deposited	1300	10 min.	<57	0.224	179	210	226	352	457	562	224	38.4
6		—1400											
7	Grade "A"	500	5 hrs.	81	0.175	194	223	228	306	376	514	208	34.7
8	Electrolytic	900	1 hr.	<57	0.175	176	211	226	352	449	547	195	32.5
0	Nickel,	1300	10 min.	<57	0.175	177	222	226	360	445	531	171	28.5
	wrought and recrystallized	—1400											

*68 Per Cent.

time of 69 per cent reduction of thickness, reduced the final thickness to 0.175 inch. Then the specimen was sawed into 3 pieces for annealing at 500, 900 and 1300 degrees Cent. (930, 1650 and 2370 degrees Fahr.).

(II) The as-deposited electrolytic nickel, grade "A", was provided with smooth upper and lower surfaces by milling to a thickness of 0.224 inch and was then cut into 4 pieces.

(III) From the same stock a sample was cold-rolled 30 per cent to 0.175 inch thickness and divided into three pieces.

One section each of the 69 per cent cold-rolled carbonyl nickel powder metal, of the as-deposited electrolytic nickel and of the 30 per cent cold-rolled electrolytic nickel was annealed in hydrogen for 5 hours at 500 degrees Cent. (930 degrees Fahr.). The annealing temperature was attained in 1 hour; the furnace cooling took 3 hours.

A second set of samples was heated in flowing hydrogen in 1¾ hours to 900 degrees Cent. (1650 degrees Fahr.), held at temperature for 1 hour and furnace cooled in 1¾ hours.

In order to produce a coarse grain material, samples from the 3 kinds of nickel were individually exposed by induction heating in hydrogen to extreme temperatures of 1300 to 1400 degrees Cent. (2370 to 2550 degrees Fahr.) briefly called in the following the "1300 degrees Cent.-anneal" (Table V, column 3).

The variations in grain size produced by the annealing treatments at 500, 900 and 1300 degrees Cent. (930, 1650 and 2370 degrees Fahr.), are shown in Figs. 7, 8, 9 for the carbonyl nickel powder metal, in Figs. 11, 12, 13 for the as-deposited electrolytic nickel and in Figs. 14, 15, 16 for the cold-rolled and recrystallized electrolytic nickel. Fig. 10 shows the microstructure of the electrolytic nickel in the electrodeposited state. Most magnifications were made at 100 diameters. Figs. 7a and 11a were made at 200 diameters. A 50/50 solution of nitric and glacial acetic acid was used for etching.

In the carbonyl nickel powder samples, recrystallization has taken place at 500 degrees Cent. accompanied by a drop of hardness from about 240 Brinell to 96 Brinell. Fig. 7a shows more clearly at 200 magnification the recrystallized grain. The 1-hour anneal at 900 degrees Cent. (1650 degrees Fahr.) produced but little grain growth (Fig. 8), the latter being impeded by the presence of impurities at the grain boundaries. (3) The further softening by 18 Brinell at 900 degrees Cent. (1650 degrees Fahr.) in comparison with the 500 degrees Cent. (930 degrees Fahr.) anneal may be largely attributed

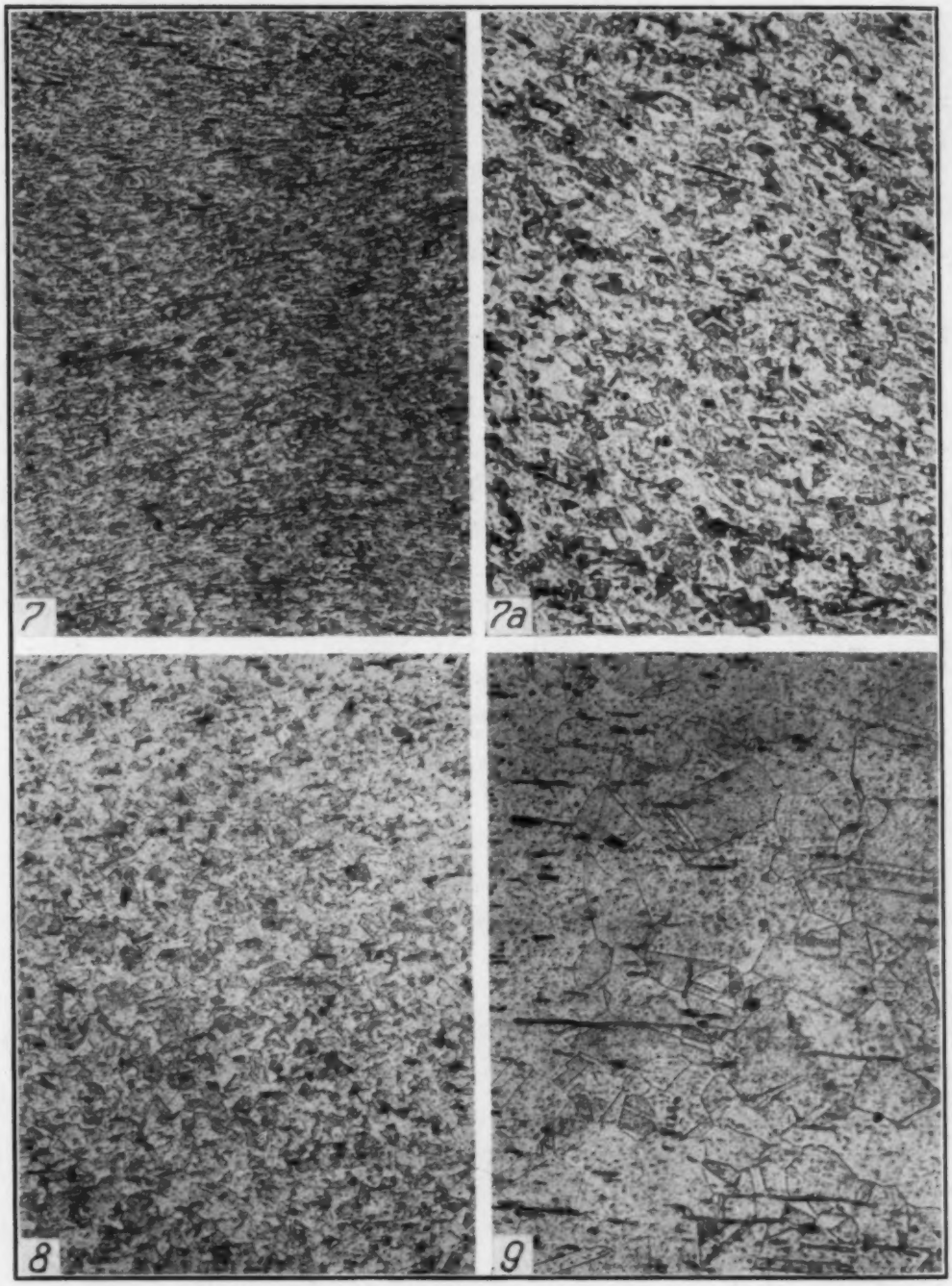

Fig. 7—Carbonyl Powder Nickel, Annealed at 500 Degrees Cent. (930 Degrees Fahr.). × 100.

Fig. 7a—Carbonyl Powder Nickel, Annealed at 500 Degrees Cent. (930 Degrees Fahr.). × 200.

Fig. 8—Carbonyl Powder Nickel, Annealed at 900 Degrees Cent. (1650 Degrees Fahr.). × 100

Fig. 9—Carbonyl Powder Nickel, Annealed at Above 1300 Degrees Cent. (2370 Degrees Fahr.). × 100.

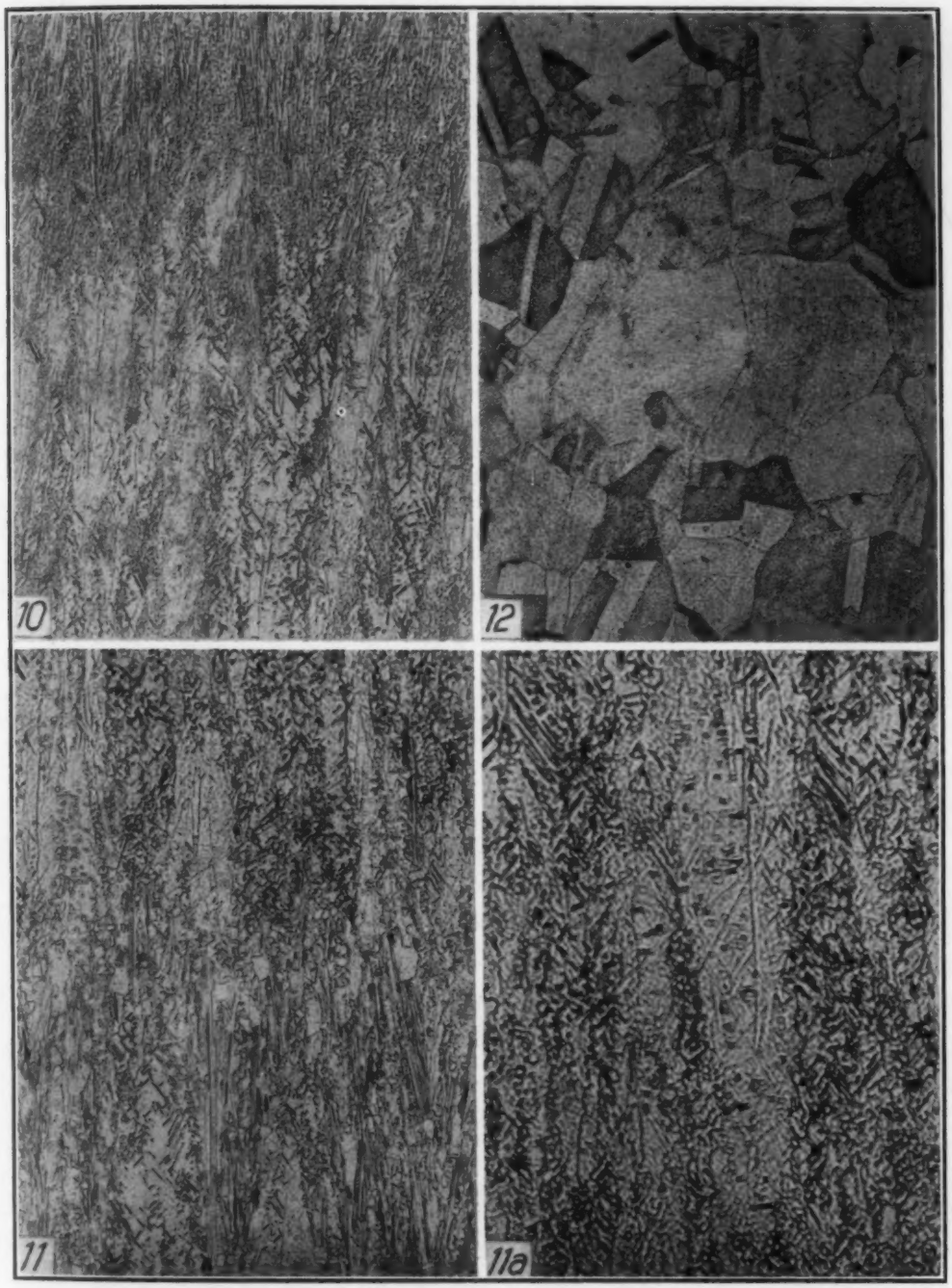

Fig. 10—Electrolytic Nickel As-Deposited. × 100.

Fig. 11—Electrolytic Nickel, Annealed at 500 Degrees Cent. (930 Degrees Fahr.). × 100.

Fig. 11a—Electrolytic Nickel, Annealed at 500 Degrees Cent. (930 Degrees Fahr.). × 200.

Fig. 12—Electrolytic Nickel, Annealed at 900 Degrees Cent. (1650 Degrees Fahr.). × 100.

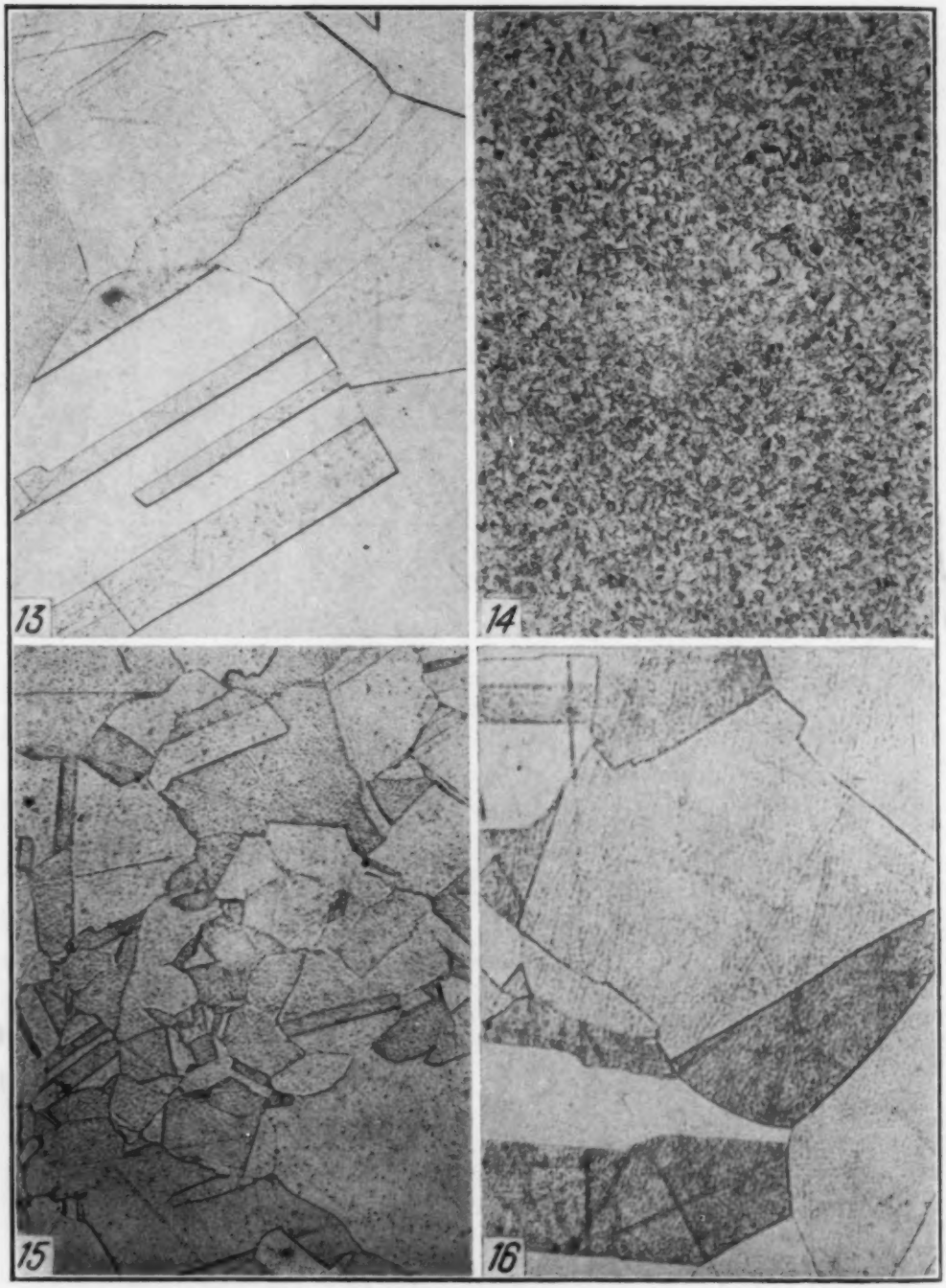

Fig. 13—Electrolytic Nickel, Annealed at Above 1300 Degrees Cent. (2370 Degrees Fahr.). × 100.

Fig. 14—Electrolytic Nickel, Cold-Rolled and Annealed at 500 Degrees Cent. (930 Degrees Fahr.). × 100.

Fig. 15—Electrolytic Nickel, Cold-Rolled and Annealed at 900 Degrees Cent. (1650 Degrees Fahr.). × 100.

Fig. 16—Electrolytic Nickel, Cold-Rolled and Annealed at Above 1300 Degrees Cent. (2370 Degrees Fahr.). × 100.

to grain growth. A marked increase of grain size occurred during the annealing at over 1300 degrees Cent. (2370 degrees Fahr.). The microstructure in Fig. 9 shows voids (and oxides?). The hardness dropped to 64 Brinell.

The microstructure of the as-deposited electrolytic nickel (Fig. 8) has apparently not been affected by the 5-hour anneal at 500 degrees Cent. (930 degrees Fahr.) (Fig. 11). This is brought out more clearly by Fig. 11a taken at 200 magnification, and showing a pronounced fibrous structure with the grains elongated in the direction of growth, that is, perpendicular to the surface of the base. Despite the absence of structural changes, the hardness dropped from 208 Brinell to 117 Brinell. Annealing at 900 degrees Cent. (1650 degrees Fahr.) (Fig. 12) abolished the structure of electrodeposition. The grains have become approximately equiaxed. Above 1300 degrees Cent. (2370 degrees Fahr.) (Fig. 13) abnormally large grain developed. The hardness at 900 and 1300 degrees Cent. (1650 and 2370 degrees Fahr.) respectively dropped to 60 RS-15T and 55 RS-15T which falls outside of the range given in the Rockwell-Brinell conversion table, the lowest Brinell hardness of which is 53 Brinell corresponding to a Rockwell superficial hardness of 61 RS-15T.

The 30 per cent cold-rolled, electrolytic nickel apparently recrystallized during the 5-hour anneal at 500 degrees Cent. (930 degrees Fahr.) as shown by Fig. 14. Neither the rolling texture of elongated grains nor the "streaky" appearance of electrodeposition is noticeable any more. The effect on microstructure of the electrolytic origin has apparently been abolished. The grain growth during annealing at 900 degrees Cent. (1650 degrees Fahr.) (Fig. 15) and above 1300 degrees Cent. (2370 degrees Fahr.) (Fig. 16) is about the same as in the nickel used in the electrodeposited state (Figs. 12 and 13).

It may be said in summary that nickel samples of the same chemical analysis but of greatly varying grain size have been obtained by thermal pretreatment at 500, 900 and 1300 degrees Cent. (930, 1650 and 2370 degrees Fahr.).

All 10 variously pretreated nickel specimens were now given reductions of thickness of about 30, 60 and 90 per cent. The recovery from these three degrees of plastic deformation was determined by heating separate samples at 13 different temperatures in the range of 192 to 605 degrees Cent. (384 to 1121 degrees Fahr.) and by determining the changes of hardness.

Results

The effect of rolling 30 to 90 per cent and of subsequent annealing is shown for the carbonyl powder metal in Figs. 17 (500 degrees Cent.), 18 (900 degrees Cent.) and 19 (1300 degrees Cent.), and for the rolled and recrystallized nickel in Figs. 24 (500 degrees Cent.), 25 (900 degrees Cent.) and 26 (1300 degrees Cent.). Figs. 20, 21, 22, 23 show the work hardening and recovery characteristics of electrolytic nickel as deposited and after the 500, 900 and 1300 degrees Cent. (930, 1650 and 2370 degrees Fahr.) anneal respectively. Each figure comprises 3 sections respectively showing a, the relation of strain hardening to the amount of plastic deformation; b, the relation of recovery of hardness from cold working to annealing temperature and to amount of reduction in thickness; and c, the

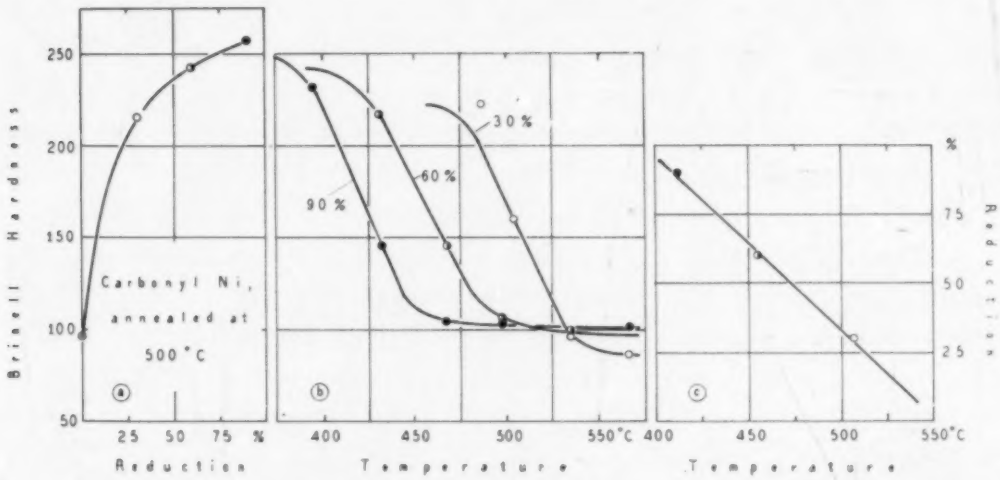

Fig. 17—Recovery of Carbonyl Powder Nickel, Preannealed at 500 Degrees Cent.

recovery temperature values T_r derived from the individual softening curves of section b. The hardness after reductions of 30, 60 and 90 per cent varies depending on the preanneal as shown by the strain hardening curves and in Table V. In the electrodeposited nickel samples work hardness is superposed on greatly varying initial or residual hardnesses due to electrodeposition. The larger the grain, and the lower the initial hardness, the smaller the work hardening and the lower the final hardness at any reduction.

The recovery temperatures T_r are given in Table V. In order to facilitate a comparison, the T_r/per cent reduction relationships found for the 500, 900 and 1300 degrees Cent. (930, 1650 and 2370 degrees Fahr.) anneal are summarized in Figs. 27, 28 and 29 respec-

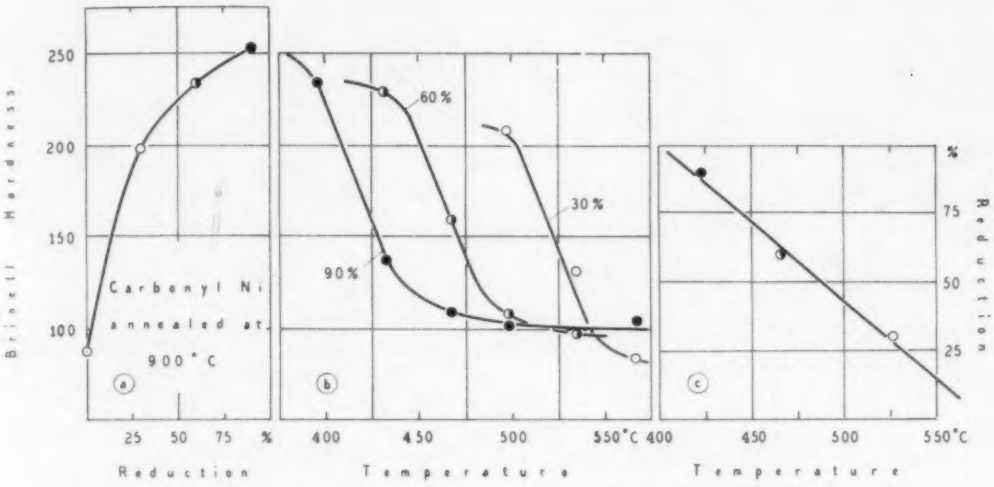

Fig. 18—Recovery of Carbonyl Powder Nickel, Preannealed at 900 Degrees Cent.

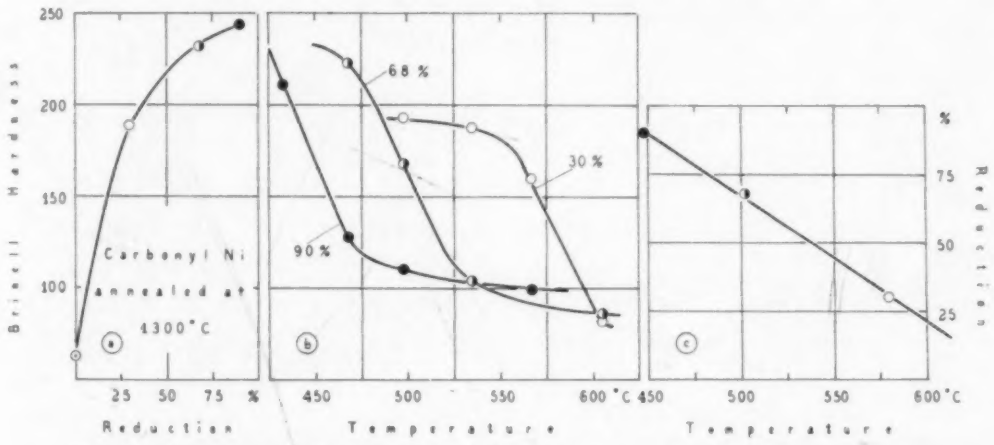

Fig. 19—Recovery of Carbonyl Powder Nickel, Preannealed at Above 1300 Degrees Cent.

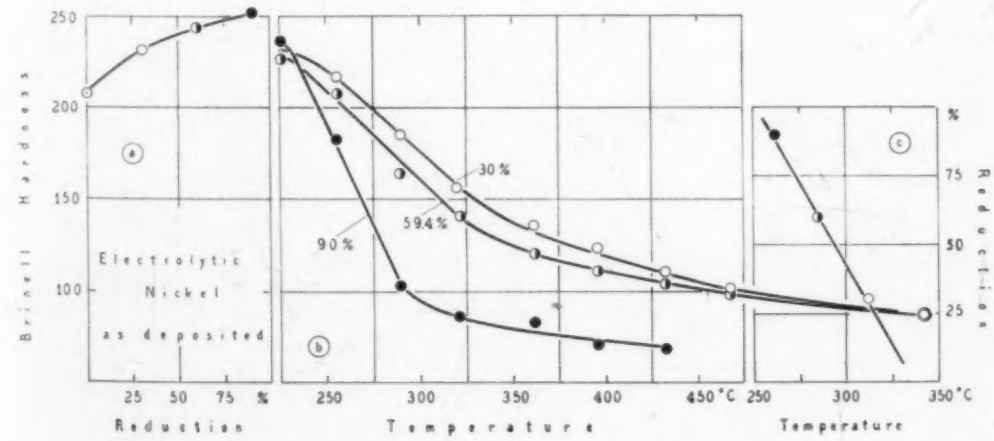

Fig. 20—Recovery of As-Deposited Electrolytic Nickel.

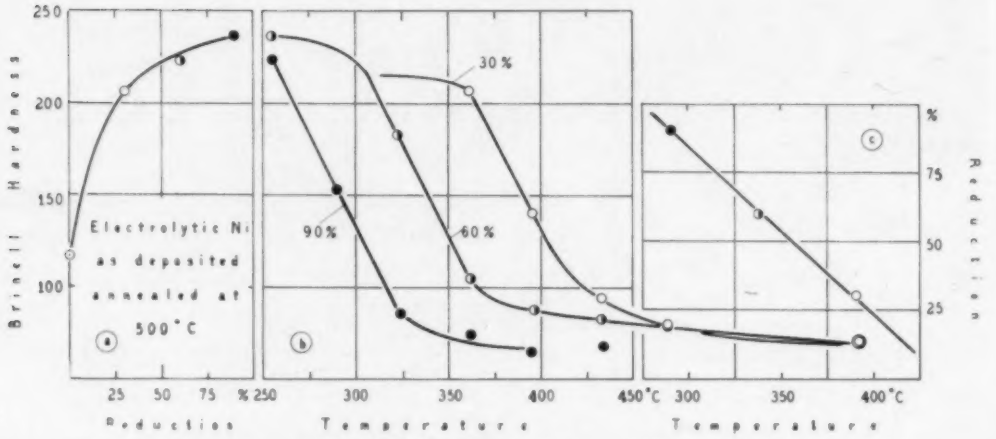

Fig. 21—Recovery of Electrolytic Nickel, Preannealed at 500 Degrees Cent.

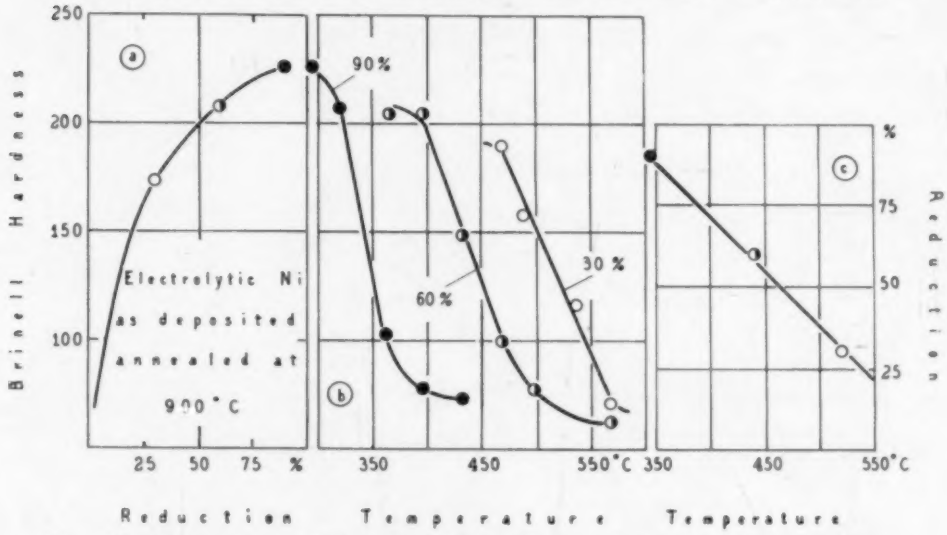

Fig. 22—Recovery of Electrolytic Nickel, Preannealed at 900 Degrees Cent.

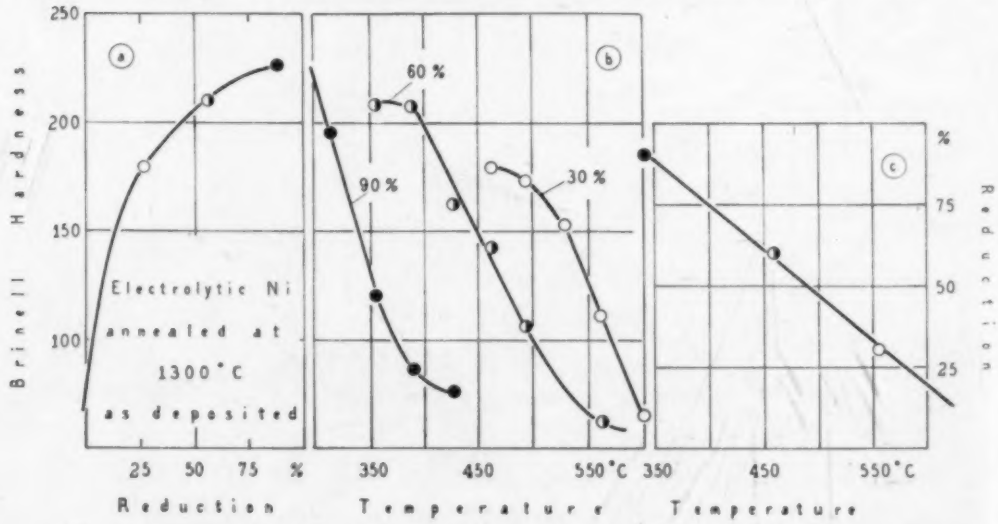

Fig. 23—Recovery of Electrolytic Nickel, Preannealed at Above 1300 Degrees Cent.

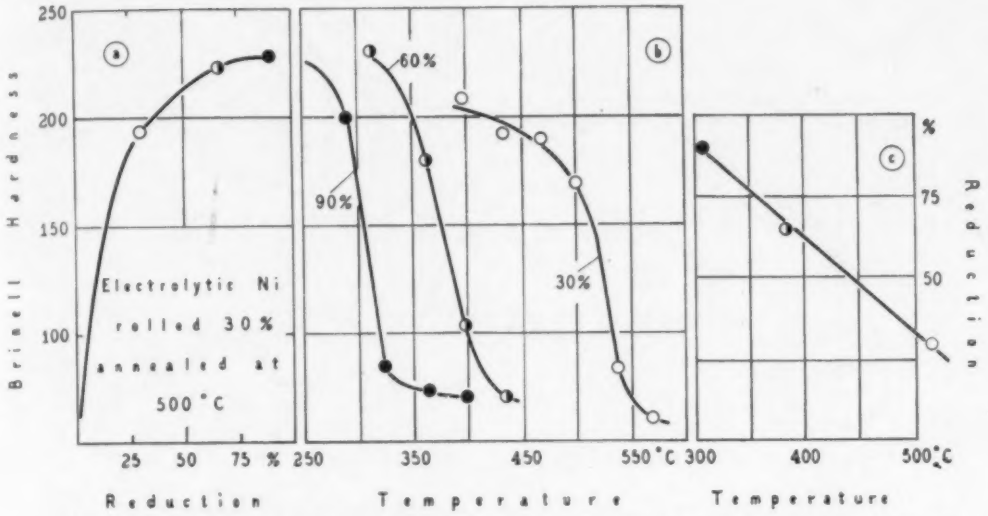

Fig. 24—Recovery of Electrolytic Nickel, Cold-Rolled and Preannealed at 500 Degrees Cent.

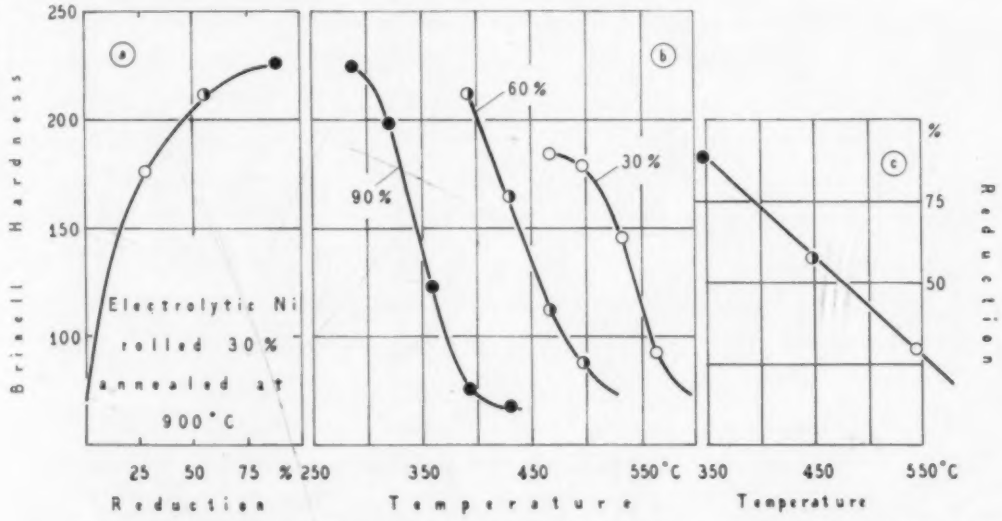

Fig. 25—Recovery of Electrolytic Nickel, Cold-Rolled and Preannealed at 900 Degrees Cent.

tively for the carbonyl powder metal, as-deposited electrolytic nickel and cold-worked and recrystallized electrolytic nickel. The Brinell hardnesses (H_B) prior to rolling are included in each diagram.

The most surprising result is that the softening range of each of the 3 materials investigated varies more or less considerably in relation to the thermal pretreatment. In the carbonyl powder metal (Fig. 27) the softening range is shifted to slightly higher temperatures by raising the preannealing temperature from 500 to 900 degrees Cent. (930 to 1650 degrees Fahr.). A pronounced shift took place with the material preannealed at about 1300 degrees Cent. (2370 degrees Fahr.). This shift of the recovery temperature range appar-

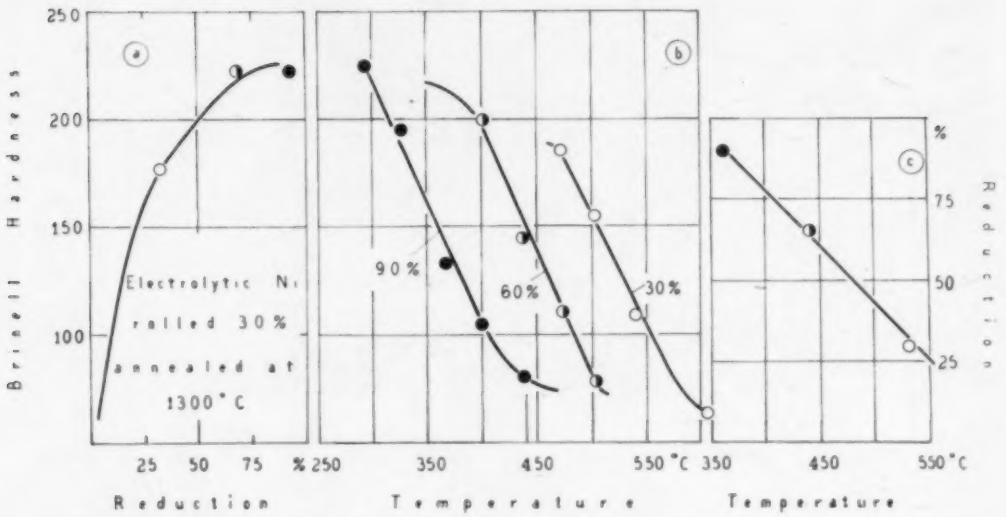

Fig. 26—Recovery of Electrolytic Nickel, Cold-Rolled and Preannealed at Above 1300 Degrees Cent.

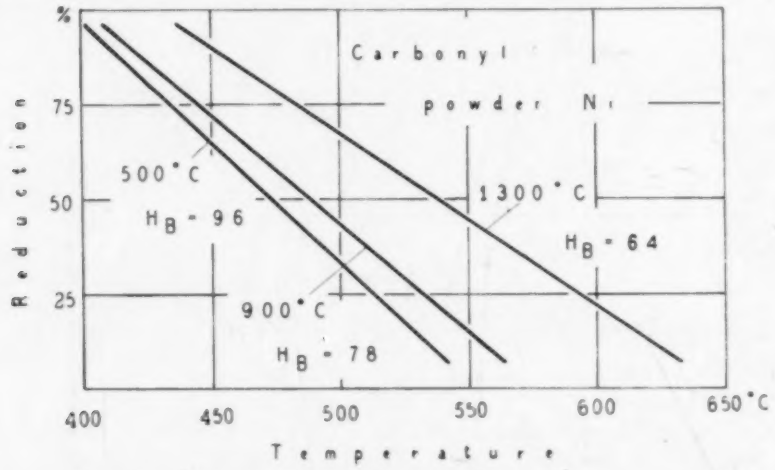

Fig. 27—Temperature Range of Hardness Recovery of Carbonyl Powder Nickel, Preannealed at 500, 900 and Above 1300 Degrees Cent.

ently has no direct relation to the residual hardness and is the greater the smaller the amount of plastic deformation. For instance, a sample preannealed at 500 degrees Cent. and then cold-rolled 90 per cent recovers at 410 and at 450 degrees Cent. (770 and 840 degrees Fahr.), or at a 40 degrees Cent. higher temperature when preannealed at about 1300 degrees Cent. With the same thermal pretreatments of 500 and 1300 degrees Cent. (930 and 2370 degrees Fahr.), the recovery temperature shifts from 537 to 627 degrees Cent. (1000 to 1160 degrees Fahr.) or by 90 degrees Cent. after a plastic deformation of only 10 per cent (extrapolated).

In the case of electrodeposited nickel, the change of the inclina-

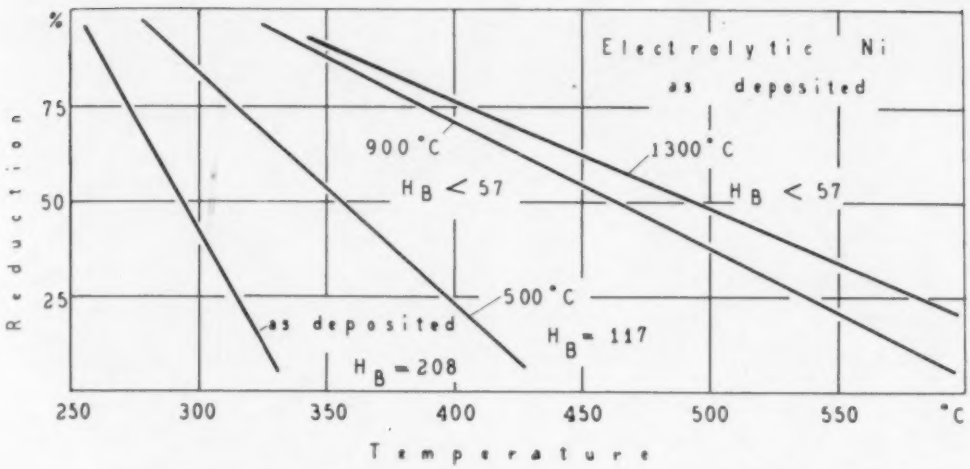

Fig. 28—Temperature Range of Hardness Recovery of Electrolytic Nickel, As-Deposited and Preannealed at 500, 900 and Above 1300 Degrees Cent.

tion of the T_r/per cent reduction curve with rising preannealing temperatures is most astounding (Fig. 28). The derived recovery temperatures of the 30 and 60 per cent cold-rolled nickel in the as-deposited state depend somewhat on the assumed "final hardness". The softening curves are markedly different from all others. The release of electrodeposition plus work-hardness takes place at a rather slow rate. Then the hardness remains practically constant over an extended temperature range. This latter hardness has been used for deriving T_r, as the further drop of hardness at much higher temperatures must be primarily attributed to grain growth.

With 10 per cent cold-rolled nickel of the same chemical analysis the recovery temperature shifts from 422 to 635 degrees Cent. (795 to 1175 degrees Fahr.) or by over 200 degrees Cent. by raising the preannealing temperature from 500 to 1300 degrees Cent. (930 to 2370 degrees Fahr.). Thus the factor of thermal pretreatment assumes a significance comparable to the drastic effect of impurities on recovery. The importance of the internal state and microstructure becomes even more apparent, when comparing the as-deposited 10 per cent cold-worked material with the same nickel annealed at 1300 degrees Cent. (2370 degrees Fahr.) prior to a 10 per cent reduction. The recovery temperature is raised by 316 degrees Cent. The shifting of the recovery temperature is less conspicuous for severe plastic deformations. The 90 per cent cold-rolled material in the as-deposited state recovers at 260 and at 353 degrees Cent. (500 and 670 degrees Fahr.) if preannealed at 1300 degrees Cent. (2370 degrees Fahr.). The extension of the softening temperature ranges of the

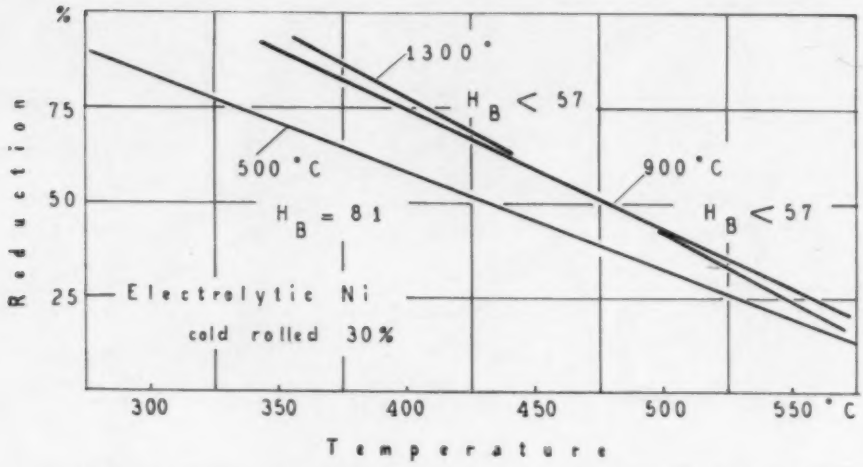

Fig. 29—Temperature Range of Hardness Recovery of Electrolytic Nickel, Cold-Rolled and Preannealed at 500, 900 and Above 1300 Degrees Cent.

electrodeposited nickel, as well as of the carbonyl powder metal is progressively enlarged with rising annealing temperatures prior to the plastic deformation.

This behavior is not confirmed with the wrought and recrystallized electrolytic nickel (Fig. 29, Table V, last column).

However, a pronounced shift of the recovery temperature range to higher temperatures is also observed when raising the preannealing temperature from 500 to 900 degrees Cent. or 1300 degrees Cent. (930, 1650 and 2370 degrees Fahr.).

Discussion

All 3 series of recovery tests prove that the internal structure or state of the tested material may profoundly affect the characteristics of hardness recovery of metal of the same chemical composition and submitted to the same cold working and annealing treatment.

This surprising finding tends to complicate the scientific establishment of recovery data as it would necessitate a characterization of the internal state of the testing material prior to plastic deformation. Such an enterprise will meet with considerable difficulties. Obviously the hardness prior to cold working is no quantitative measure of the internal state of the metal. Grain size appears to play an important rôle. It may be deduced in general, that the recovery temperature is the higher the larger the grain.

It appears plausible that initial strains before cold working—as qualitatively expressed by a greater hardness—would add to the amount of induced cold working energy, increase the vibration ampli-

tude of the atoms in the space lattice and lower the softening and recrystallization temperatures. Besides this, a fine grain material presumably absorbs a larger amount of cold working energy than a large grain one as indicated by the powder metal and electrodeposited nickel.

An interpretation of the remarkable shift of the recovery temperature range of the as-deposited electrolytic nickel is difficult insofar as the true nature of the electrodeposition hardness is not known yet, although the conditions for obtaining hard nickel deposits such as current density, temperature, hydrogen ion concentration, addition of boric acid, ammonium sulfate or chloride are well understood. (12), (25). There is much evidence against the hydrogen theory, (26), (27). It is generally agreed that the electrodeposition hardness is the higher the finer the grain. The latter is attributed to interferences with crystal growth exerted by colloidal nickel hydroxide or other basic compounds which are precipitated in the film of solution or the cathode surface and are occluded in the deposit (12), (13). Whether the electrodeposition hardness is solely controlled by grain size or is increased by the presence of nonmetallic particles in a critical state of dispersion has not been established. However, the electrodeposited nickel seems to be in a condition of high internal stress to which the working stresses are added resulting in a lowering of the recovery temperatures. The markedly different course of the softening curve of 30 and 60 per cent cold-worked as-deposited nickel may be an indication that work hardness and electrodeposition hardness are of a different nature.

The shifting of the recovery temperature range (Fig. 28) is not directly related to the initial hardness prior to rolling. Obviously the grain size plays an additional rôle. This had also been previously indicated by experiments with carbonyl nickel powder metal (2). By increasing the number of plastic deformations and recrystallizations in hydrogen and thus obliterating the effect of the origin as powder metal, the recovery temperature range progressively shifted to higher temperatures, in spite of the counteracting effect of purification owing to the long-time intermediary anneals in hydrogen.

One problem that has never been attacked is why the extension of the recovery temperature of variously deformed nickel changes with material of the same chemical analysis. An answer seems to be furnished by these experiments, in particular by Figs. 27 and 28. The internal structure and state of the tested material prior to cold

working obviously affects the inclination of the T_r/per cent reduction curve. But why are differences in recovery temperature less pronounced with severely deformed material? It appears that there is a maximum of cold work energy which can be stored in metallic materials. Hardness or tensile strength curves flatten out more and more towards maximum plastic deformations. If there are initial stresses in a certain material, its absorption of further stresses induced by cold working should be more limited than with the same material in the unstrained state. For instance, in the hard electrodeposited nickel the absorption power of further strains or the additional storage of internal energy is soon exhausted. The hardness increases only from 208 Brinell to 252 Brinell by 90 per cent cold rolling. The recovery at severe and moderate plastic deformation occurs in this initially highly strained material at temperatures which lie more closely together than with the same material fully annealed and able to absorb more and more cold work energy as the plastic deformation continues, striving towards the maximum of absorption power. Therefore, the recovery temperatures of all severely deformed specimens fall more or less closely together.

The problem seems to be complicated by the effect of grain size. Metal in the fine grain state is harder than in the coarse grain. This is attributed to slip interference at the grain boundaries. Yamaguchi (28) even advances a theory that work hardening is caused by work hardening at the boundaries of the grains which are continuously broken up with progressive plastic deformation. Seumel (29) proved microscopically that the density of the slip planes decreases towards the grain boundary and X-rays indicate changes of crystal orientation near grain boundaries.

It thus appears that plastic deformation, amount of stored latent energy and recovery from cold working should depend on grain size, i.e., on the "internal surface" of the metal. Apparently more cold work energy is absorbed at the grain boundaries than within the grains. Experiments on aluminum, brass and aluminum-zinc disclosed that recrystallization begins at the boundaries of the old distorted crystals (30), (31). Recrystallization nuclei are points of maximum lattice disturbance (32). It had been previously demonstrated by the author (3), (4), (5) that fine grain powder metal plastically deformed in the unstrained soft state recrystallizes and recovers from work hardening at remarkably low temperatures.

It is possible that the recovery temperatures reported above on

the severely cold-worked as-deposited nickel would have been even lowered if electrolytic nickel had been employed that had a greater electrodeposition hardness than 208 Brinell and which still could lend itself to plastic deformation. Differences in the recovery characteristics of electrolytic nickel are bound to show up as is already indicated by experiments by Wazau (33). Although applying long annealing times of 5 hours and the drastic method of cold working by upsetting, Wazau found the high recovery temperature of T_r = 570 degrees Cent. for as-electrodeposited nickel plastically deformed 20 per cent. This recovery temperature is much higher than found by the present author on electrodeposited nickel. The chemical composition of the testing material used by Wazau is not given. Although the grades of electrolytic nickel of 1924 are presumably less "pure" than the latest highly pure grades, the proof is lacking whether metallic impurities in electrodeposited metals have the same sometimes exceedingly drastic effect upon recovery from cold working as in ordinary solidified metals. With increasing amounts of finely dispersed colloidal impurities these effects have been observed: grain size diminishes, hardness increases, softening is shifted to lower temperatures, (34) microstructural changes are shifted to higher temperatures in the as-deposited state (13), and, if cold-worked, recovery and recrystallization temperatures are lowered (3), (4), (5).

The same phenomenal lowering of recrystallization and hardness recovery temperature ranges were observed in cold-worked compressed carbonyl nickel powder metal as well as in cold-worked electrolytic nickel. Both metals have not passed the liquid state and have certain structural features in common. It remains to be seen whether the above described drastic effect of thermal pretreatment on the recovery characteristics has the same significance in regard to ordinary, solidified metals or whether it constitutes another phenomenon characteristic of powder metals and not reproducible in metals which have passed through the liquid state (35). In view of the rapidly expanding field of powder metallurgy, the findings of this investigation appear to have both, scientific and commercial significance.

Summary

Considerable differences between recovery of work hardness at the surface and in the interior regions of fine and coarse grain nickel cold-rolled 10 and 25 per cent were found. No general correlation

of work hardening to recovery temperature seem to exist. In view of the variations from spot to spot and of the varying degree of penetration in hardness tests, the application of hardness testing for determination of recovery data appears inadvisable with reference to small plastic deformations. However, recovery tests offer a sensitive method of determining the uneven effects of plastic deformation throughout the testing material at small plastic deformations.

A profound effect of thermal treatment prior to plastic deformation on both the extension and location of the recovery temperature range was found with carbonyl powder nickel, as-deposited electrolytic nickel and cold-worked and recrystallized electrolytic nickel. Material of the same composition, cold-rolled to the same extent and annealed at the same temperature for the same length of time, was found to lose its work hardness at different temperatures depending on the annealing treatment prior to the plastic deformation. This effect is attributed to grain size and residual stresses prior to cold working. The effect of thermal pretreatment on the characteristics of recovery is least pronounced at severe plastic deformations and greatest at small ones. A characterization of the internal state (microstructure, strains), of material submitted to recovery tests appears to be mandatory.

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DISCUSSION

Written Discussion: By C. G. Goetzel, assistant director of research, American Electro Metal Corp., Yonkers, N. Y.

Mr. Fetz's investigation is very interesting indeed, particularly the part dealing with experiments on carbonyl nickel powder metal. This research constitutes another valuable contribution to the methodic study of metals prepared by powder metallurgical processes.

However, the fact that the metal obtained from carbonyl powder appears to be somewhat contaminated by pores and impurities, probably oxide, as is indicated by the photomicrographs, Figs. 7 to 9, is rather surprising. In order to form streak-like agglomeration of inclusions, the amount of impurities in the carbonyl powder metal must be considerable. This is rather inconceivable since carbonyl metal powders are generally considered to be of highest purity. Besides, the intense heat treatment given to the metal during its processing should be expected to remove the impurities to some extent.

It must be borne in mind that such inclusions have a definite bearing on grain size and physical properties of the metal, and, therefore, it must be assumed that different results might have been obtained with a carbonyl nickel, essentially free from impurities.

It would be interesting if a chemical analysis of the carbonyl nickel powder and of the wrought metal could be made, particularly with regard to the oxygen content.

It also would be interesting indeed if the author could add to his otherwise so complete investigation a few tests with purified carbonyl nickel powder and with another type of nickel powder, such as obtained from nickel oxalate or by electrolysis. Purification of the carbonyl powder by hydrogen reduction at temperatures in the neighborhood of 600 degrees Cent. and subsequent heating and cooling in vacuum for degassing purposes might well result in a much purer metal and consequently in somewhat different results of the recovery experiments.

Written Discussion: By N. P. Goss, physicist, Cold Metal Process Co., Youngstown, Ohio.

The author has presented very interesting data showing that the initial state or the pretreatment given a specimen of nickel exerts a profound influence upon the recovery temperature preceded by cold working.

On page 236 the author points out that the difference in recovery temperature is less pronounced in severely deformed material, due to the fact that a metal can only absorb a definite maximum of energy by cold working. Also that hard electrodeposited nickel can only be hardened from 208 Brinell to 252 by a 90 per cent cold reduction. These and other experimental observations made by the author clearly show that hardening and recovery are related to the internal structure of the grains.

X-ray diffraction has conclusively shown that cold working fragments

the grains into smaller crystallites, differing in orientation from the parent grain. The orientation of the crystallites may vary from seconds of arc to many degrees. I have been able to show that even the severest cold working does not fragment the grain without limit, but only into crystallites about 10^{-5} cm. in magnitude. Recent work by Wood, Kornfeld and others supports this.

The energy content of a particle depends upon its size. A particle of colloidal dimensions should have the maximum energy content. However, the severest cold working cannot reduce the crystallite size to colloidal dimensions. This explains why cold working cannot harden a metal beyond a fixed limit regardless of how severe the cold working may be.

In the hard electrolytic nickel deposits, the particle size is already small, and further cold working does not fragment them appreciably. This would account for the small increase in hardness.

It is also well known that changes in the physical properties occur below recrystallization temperatures. X-ray diffraction patterns of severely worked metals heat treated below recrystallization temperatures show a progressive sharpening of the diffraction pattern. This is attributed to a slight increase in the particle size, which cannot be observed under the microscope. This recovery can only occur when the particles which differ but slightly in orientation from each other combine to form a larger particle. After combining they have the same orientations, and therefore such recovered particles have a lower energy content. Such changes which take place below recrystallization temperatures have been referred to as recovery, healing, etc. In other words, the internal surface is decreased, thus causing a slight change in the hardness, strength and dimensions of the specimen, etc.

It is also apparent that the smaller the crystallite size the lower the recovery temperature will be. Also the power to recrystallize is not altered by these recovery effects. Therefore recovery precedes recrystallization.

Recrystallization as observed under the microscope can only take place at higher temperatures, because greater forces are required to reorient the crystallites which differ greatly in orientation from each other so that they will have the same orientation as the growing grain which has absorbed them. One phase of the phenomena of grain growth must be a process of rotation of the crystallites, so that they assume the same orientation as the nucleus. The crystallization nucleus must therefore possess the power to reorient the crystallites.

Grain growth is therefore a process of reorienting crystallites about 10^{-5} cm. in size to assume the same orientation as the nucleus. The crystallite or block never loses its identity.

Cold working is the reverse of this process, in that the crystallites within the grains (inherently) are caused to rotate into new orientations. The new orientation of the crystallites after deformation may vary only a few seconds of arc to several degrees of arc from the parent grain.

The crystallites which differ but slightly in orientation from each other and are small enough may combine to form larger particles by thermal treatment below recrystallization temperatures. These changes can be observed with the X-ray but not with the microscope.

Author's Reply

I should like to thank Messrs. Goss and Goetzel for their interest taken in this paper and for their pertinent discussions: Mr. Goss's statement that "recovery precedes recrystallization" seems to contradict at first sight former conclusions (3).[1] However, there is only a difference in terminology. What Mr. Goss calls "recovery" are some changes visible by, and only by, X-rays. When I refer to recovery, I mean any change of physical properties of cold-worked metal due to annealing. It has been observed by Tammann and co-workers that this restoration of the physical properties of the annealed state may take place in widely different temperature ranges for different physical properties of the same metal. (*Zeitschrift für Metallkunde*, Vol. 26, 1934, p. 97; Vol. 28, 1936, p. 6).

I personally have been interested for several years (1-5) in the abolition of the cold work hardness and of the deformation texture on annealing as both properties attract technological and scientific interest. With reference to the hardness recovery data reported in this paper, it was observed that microscopic recrystallization takes place in the same temperature range as the hardness recovery or the release of work plus electro-deposition hardness (5). Mr. Goss's observation that incipient recrystallization can be noticed by X-rays before any microscopic changes occur has also been reported by other experimenters and has occasionally been referred to as "healing" or "relaxation." These differences are probably attributable in part to the dimensional differences in the resolving power of X-rays as compared with visible light waves.

The interpretation of changes in Laue patterns and sharpening of X-ray diffraction lines on annealing cold-worked metals still seems to be a rather controversial subject. It is interesting to learn from Mr. Goss's experiments that the sharpness of the outermost diffraction lines may also depend on the choice of the wave length of the X-rays used. Another interesting case relating to the effect of the testing conditions on the sharpness of the diffraction lines was reported several years ago before this Society proving that the diffraction lines of aluminum were blurred when the metal was cold-rolled 60 per cent at −76 degrees Cent. (Wilson and Thomassen, TRANSACTIONS, American Society for Metals, Vol. 12, 1934, p. 19), while distinctly split $K\alpha$-doublets are obtained with aluminum rolled 90 per cent at room temperature. (Dehlinger, *Zeitschrift für Kristallographie*, Vol. 65, 1927, p. 615.) Some metals, like tantalum, show blurring of the diffraction lines after only slight deformations. Apparently, we do not completely understand as yet the significance of the changes in X-ray pictures in relation to progressive cold working and consequently the correlation of such changes to recovery phenomena meets difficulties.

Dr. Goetzel is correct that the purity of the testing material profoundly affects the recovery from cold working and that different results would have been obtained if powder material of the highest purity had been used. However, in the case of powder metals, the drastic effect of mechanical and thermal pretreatment should not be overlooked. Attention may be called to

[1]The figures appearing in parentheses refer to the bibliography appended to the paper.

previous experiments (2). Carbonyl powder nickel showed phenomenally low recovery and recrystallization temperatures after moderate plastic deformation and limited annealing treatments. By increasing the number of plastic deformations and hydrogen anneals, the recovery and recrystallization temperatures were progressively shifted to higher temperatures although the purity of the metal was certainly improved due to the reduction of oxides in the long-time hydrogen anneals at elevated temperatures. Obviously the effect of the origin of the nickel as powder metal was more pronounced than the counteracting effect of purification.

It was not the object of this investigation to study the effect of purity on recovery as this has been done previously (4). It must be admitted that the recovery temperatures of the carbonyl nickel samples are rather high in comparison with former tests, which certainly reflects on the purity of the powder used. However, the aim of this paper was to study qualitatively the effect of grain size prior to cold working on hardness recovery. In this regard it might have been advisable to extend the 1300-degree Cent. preanneal of the powder carbonyl nickel in order to produce some really large grain (Fig. 9) comparable to the exceedingly large grain obtained with the electrolytic nickel samples (Figs. 13 and 16). In this case, the hardness recovery range would probably have been shifted to temperatures still higher than shown in Fig. 19 for the 1300-degree Cent. preanneal.

Regarding the chemical composition, some typical analyses have been presented previously (4). Reference to previous work may also be made concerning Dr. Goetzel's question about the recovery of nickel obtained from powder other than nickel carbonyl (1).

EFFECTS OF SMALL AMOUNTS OF ALLOYING ELEMENTS ON THE TEMPERING OF PURE HYPEREUTECTOID STEELS

By Charles R. Austin and B. S. Norris

Abstract

The paper deals with the softening characteristics of 1.1 per cent carbon steels, made from electrolytic iron melted under hydrogen in an induction furnace, and containing ½ per cent or less of one of the following third elements: manganese, silicon, nickel, chromium, copper, aluminum, sulphur, phosphorus, or tin.

The steels were hardened and subsequently tempered for a period ranging from ½ to 125 hours at five different temperatures: 550, 590, 630, 670 and 710 degrees Cent., the reaction to heat treatment being followed by hardness determinations and metallographic study.

Approximate linear relationship exists between either Rockwell "B" or Brinell hardness and log tempering time, over a period of ½ and 125 hours, so long as graphitization does not occur. Profound graphitization occurred in some of the tempered aluminum steels.

In the alloys containing approximately ½ per cent of the added elements manganese, silicon, aluminum, or copper, after a tempering period of one hour at any of the temperatures investigated a hardness value from 10 to 30 Brinell units greater than that for the plain carbon steel was obtained. For chromium the values were 70-100 units higher, whereas nickel appeared to have little effect.

When the quantity of added element is 0.07 to 0.08 per cent only small differences existed between the hardness of the alloys and that of the carbon steels after a 1 hour temper in the temperature range studied. The effect of chromium, in such small amounts, was noteworthy.

Information pertaining to the effect of alloying elements on rate of softening at 710 degrees Cent. is presented, while a comparison is drawn between the effect of tempering temperature on the rate of softening for the nickel and for the chromium steels, containing approximately ½ per cent alloy.

A paper presented before the Twenty-second Annual Convention of the Society held in Cleveland, October 21 to 25, 1940. Of the authors, Charles R. Austin is professor of metallurgy, and B. S. Norris is graduate assistant in metallurgy, Pennsylvania State College, State College, Pa. Manuscript received July 6, 1940.

IN a recent paper (1)[1] by the authors, attention was directed to the importance of studies on the effects of tempering hypereutectoid steels, and a critical review of the literature provided information dealing with reactions occurring in carbon steels below the eutectoid. The paper illustrated the difference in reaction to tempering, of commercial hypereutectoid carbon steels of "similar chemical composition," after quenching from 1000 degrees Cent. (1830 degrees Fahr.), with particular reference to tendency to partial or complete graphitization at certain subcritical temperatures.

In an attempt to evaluate more clearly the role of the usual commercial impurities found in carbon steels, on their reaction to heat treatment a series of pure iron-carbon alloys were prepared containing small amounts of one added element. Relatively little quantitative information is available in the literature on the effect of small amounts of such elements on the heat treating characteristics, although difference in behavior of "similar" steels is usually ascribed to the small difference in alloy content.

In the cited paper by the authors (1) as well as in later investigations (2), (3), attention was directed to the marked difference in susceptibility to graphitization in the steels of so-called similar analyses, and the new alloys have been used to pursue further this study. However, this paper will relate more particularly to the effect of the added elements on the progress of spheriodization, as revealed by change in hardness, on tempering.

Materials and Experimental Procedure

The steels used in the present investigation were made under carefully controlled conditions at the Battelle Memorial Institute. Since it was desired to keep the impurities to a minimum, electrolytic iron and pure alloying elements were used, and melting was conducted in an induction furnace under a hydrogen atmosphere. The 7.5-pound ingots so produced were also cast under hydrogen. The authors had the advantage of the complete supervision of these preparations by Dr. C. H. Lorig.

The ingots were subsequently forged, rolled, annealed, and centerless ground to ⅜-inch bar stock, by the kind assistance of Latrobe Electric Steel Company, under the guidance of Dr. Miles

[1]The figures appearing in parentheses refer to the bibliography appended to this paper.

K. Smith. All heat treatments for forging, rolling and finishing were conducted in a reducing atmosphere.

The heats were made to analyze 1.1 per cent carbon and approximately 0.05, 0.1 and 0.5 per cent of the elements, manganese, silicon, nickel, chromium, copper, and aluminum. Since finances limited the number of alloys that could be prepared, only one sulphur, phosphorus, and tin alloy was made, with each alloy containing 0.05 per cent of the indicated element.

Table I
Chemical Composition Per Cent

Steel	Alloy	C	Mn	Si	Ni	Cr	Cu	Al	S	P	Sn
87	None	1.08	0.006	0.021	0.017	0.002	0.008	<0.005	0.015	0.012	<0.003
89	None	1.09	0.005	0.023	0.018	0.003	0.006	<0.005	0.016	0.012	<0.003
26	Al	1.12	0.005	0.03	0.015	0.003	0.009	0.012	0.015	0.014	<0.003
27	Al	1.15	0.006	0.01	0.018	0.002	0.008	0.073	0.015	0.014	<0.003
28	Al	1.14	0.006	0.015	0.015	0.002	0.011	0.37	0.014	0.014	<0.003
72	Mn	1.14	0.04	0.01	0.014	0.003	0.013	0.006	0.015	0.014	<0.003
73	Mn	1.11	0.08	0.01	0.018	0.003	0.009	0.006	0.014	0.014	<0.003
76	Mn (P)	1.10	0.24	0.015	0.013	0.002	0.004	0.007	0.017	0.031	<0.003
83	Mn	1.14	0.30	0.042	0.015	0.003	0.006	0.003	0.019	0.014	<0.003
77	Si	1.08	0.006	0.08	0.014	0.003	0.006	0.006	0.016	0.012	<0.003
29	Si	1.20	0.005	0.12	0.015	0.003	0.007	0.007	0.015	0.012	<0.003
78	Si	1.08	0.006	0.14	0.012	0.003	0.005	0.008	0.017	0.012	<0.003
79	Si	1.15	0.006	0.48	0.010	0.002	0.004	0.006	0.015	0.014	<0.003
66	Ni	1.10	0.009	0.028	0.08	0.002	0.007	<0.005	0.014	0.012	<0.003
67	Ni	1.14	0.005	0.022	0.13	0.003	0.006	0.007	0.014	0.012	<0.003
74	Ni	1.04	0.007	0.024	0.53	0.003	0.008	0.006	0.017	0.012	<0.003
82	Cr	1.07	0.004	0.033	0.015	0.07	0.004	0.003	0.018	0.014	<0.003
84	Cr	1.14	0.004	0.030	0.017	0.13	0.004	0.003	0.016	0.014	<0.003
85	Cr	1.16	0.006	0.024	0.018	0.46	0.007	<0.005	0.015	0.012	<0.003
69	Cu	1.11	0.006	0.01	0.018	0.003	0.068	<0.005	0.014	0.015	<0.003
70	Cu	1.10	0.005	0.01	0.015	0.002	0.104	<0.005	0.015	0.014	<0.003
71	Cu	1.16	0.005	0.01	0.015	0.002	0.35	0.007	0.014	0.014	<0.003
80	S	1.15	0.006	0.01	0.017	0.003	0.005	0.007	0.048	0.012	<0.003
81	Sn	1.08	0.004	0.024	0.016	0.003	0.007	0.003	0.018	0.012	0.05

To Mr. A. C. Chamberlin, Bethlehem Steel Corporation, the authors are indebted for the complete chemical analyses of the 24 alloys prepared. The quantity of the chemical elements present in the steels were determined by the usual chemical methods, with the exception of copper, aluminum, and tin which were analyzed spectroscopically. Where manganese, silicon, nickel and chromium were present only as impurities, such elements were also determined spectroscopically.

A survey of the data listed in Table I reveals that the impurities are lower in quantity than would be found in commercial steels of the same carbon content, but in Alloy 76, the 0.05 per cent phosphorus steel inadvertently, contains 0.24 per cent manganese. Naturally the synthetic compositions have been approximated only. Thus some small variations occurred in the carbon content but only four

steels show a difference greater than 0.05 per cent from the initially desired value of 1.1 per cent.

It should be noted that there are two plain carbon steels (87 and 89) of almost identical analysis. Alloy 87 was prepared as a pure iron-carbon alloy without any addition, whereas number 89 was similarly prepared, but with the addition of 0.025 per cent aluminum. Since analysis shows total aluminum less than 0.005 per cent this steel has been classed with the plain carbon steel. Alloy 29 was prepared as a 0.01 per cent aluminum alloy, but while this aluminum content was approximated, the inadvertant pickup of 0.12 per cent silicon renders necessary its classification with number 78 as a silicon alloy.

The initial hardening treatment of the alloys was obtained by annealing for 1 hour in vacuum at 1000 degrees Cent. (1830 degrees Fahr.) followed by water quench. The steels were then tem-

Table II
Austenitic Grain Size After 1 Hour at 1000° C.

Steel	Per Cent Alloy	A.S.T.M. Grain Size	Steel	Per Cent Alloy	A.S.T.M. Grain Size
87	None	3	79	0.48 Si	2 (50%) 4 (50%)
89	None	2	66	0.08 Ni	3
26	0.012 Al	2	67	0.12 Ni	3
27	0.073 Al	3	74	0.53 Ni	1
28	0.37 Al	2 (60%) 4 (40%)	82	0.07 Cr	2
			84	0.13 Cr	3
72	0.04 Mn	4	85	0.46 Cr	2½ (60%) 5 (40%)
73	0.08 Mn	1			
76	0.24 Mn (P)	1	69	0.068 Cu	2
83	0.30 Mn	2	70	0.104 Cu	1
77	0.08 Si	3½	71	0.35 Cu	1½
29	0.12 Si	2	80	0.048 S	4
78	0.14 Si	3	81	0.05 Sn	1

pered in lead covered with "lead-pot" carbon to prevent oxidization, and finally quenched in water. Tempering temperatures ranged from 550 to 710 degrees Cent. (1020 to 1310 degrees Fahr.) and time of tempering varied from ½ to 125 hours. Separate specimens were used for each test and hardness studies were made on a transverse cut of the sample.

Experimental Results

The temperature of 1000 degrees Cent. (1830 degrees Fahr.) was employed as the hardening temperature in order to effect homogenization and to obtain a more uniform austenitic grain size over the complete series of alloys. According to the results of a study made

by Steigerwalt (4) on the effect of temperature on the austenitic grain size of these alloys, it was found that the grain size was fairly uniform after a treatment of 1 hour at 1000 degrees Cent. (1830 degrees Fahr.). Some of the data are given in Table II.

The complete hardness test data obtained on the quenched and tempered samples are presented in Figs. 1 through 5. It will be noted that five different tempering temperatures were employed,

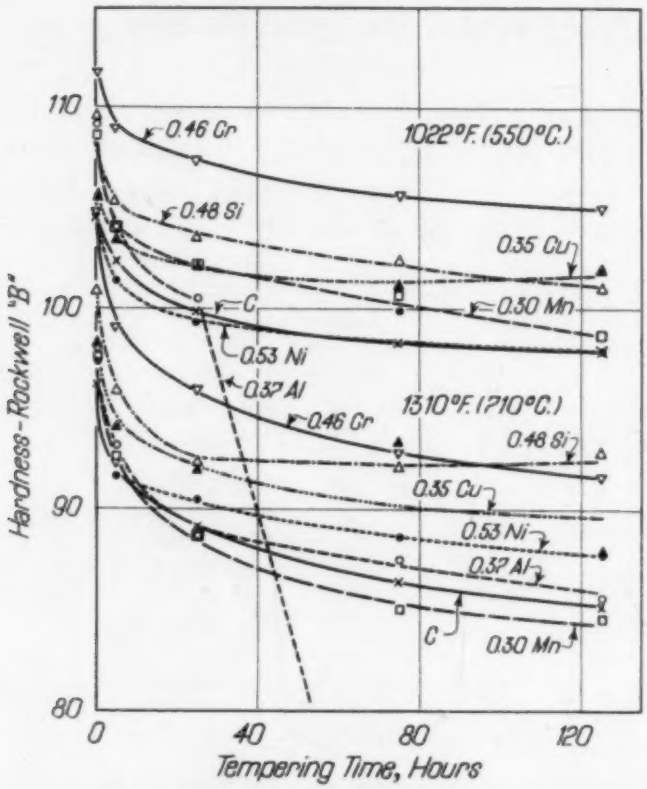

Fig. 1—Effect of Time of Tempering at 550 and 710 Degrees Cent. on Hardness of Carbon and High Alloy Steels, Containing Approximately ½ Per Cent of Added Element.

namely, 550, 590, 630, 670, and 710 degrees Cent. (1020, 1095, 1165, 1240, 1310 degrees Fahr.), and six different periods at temperature were used—½, 1, 5, 25, 75, and 125 hours.

After hardening by quenching, all steels were completely martensitic and showed a Rockwell C hardness of about 65.

Considering first the steels containing the greatest amounts of alloying element, the relation between Rockwell B hardness and tempering time, at the lowest and highest tempering temperature used, is shown in Fig. 1. One of the pure iron carbon alloys (No. 87) is

included in the graph as a basis for comparison. The most important characteristic is the fact that the alloying element has a profound effect on the relative position of the curves with respect to their hardness co-ordination. At 550 degrees Cent. (1020 degrees Fahr.) the chromium steel is markedly higher in the chart than the other alloys, while the nickel and aluminum steels follow almost exactly the behavior of the pure carbon alloy. The sudden drop in hardness

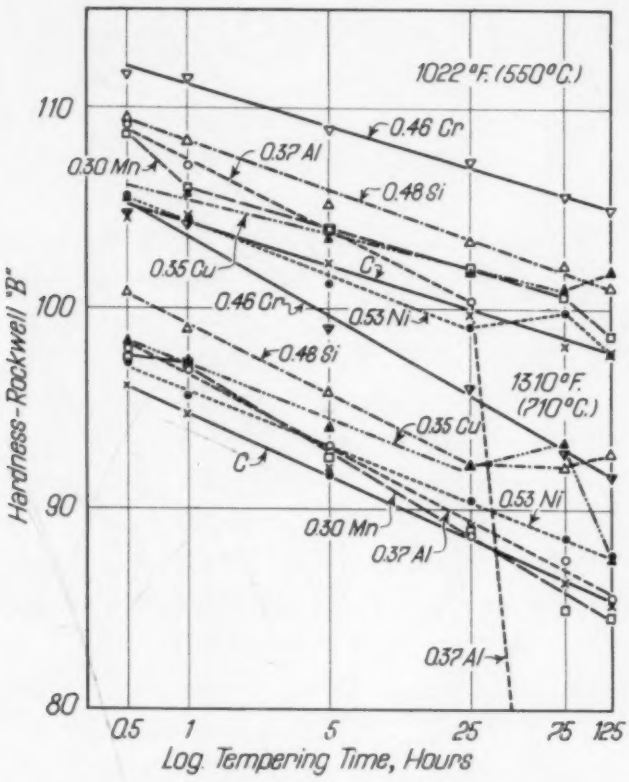

Fig. 2—Semilogarithmic Plot Showing Relation Between Hardness and Time of Tempering at 550 and 710 Degrees Cent. for Carbon and High Alloy Steels, Containing Approximately ½ Per Cent of Added Element.

of the aluminum alloy after tempering beyond 25 hours is accounted for by graphitization. The steels containing silicon, copper and manganese exhibit a reaction to softening intermediate between the noted extremes.

At 710 degrees Cent. (1310 degrees Fahr.) some changes occur in the relative position of the curves. For short periods of tempering the high chromium alloy maintains its superior position in resistance to softening by heat treatment, but after 125 hours at temperature the silicon steel shows maximum hardness. The erratic values

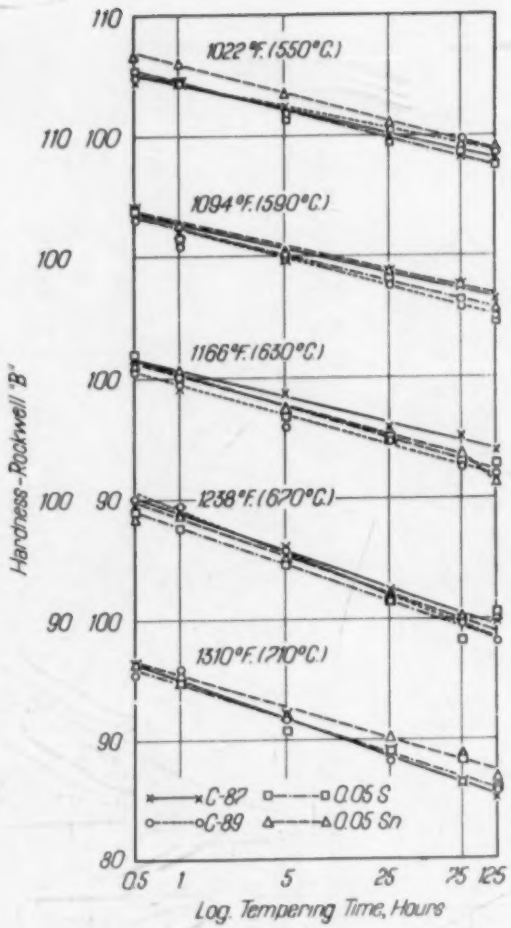

Fig. 3A—Semilogarithmic Plot Showing Relation Between Hardness and Time of Tempering at 550, 590, 630, 670 and 710 Degrees Cent. for the Carbon, Sulphur and Tin Steels.

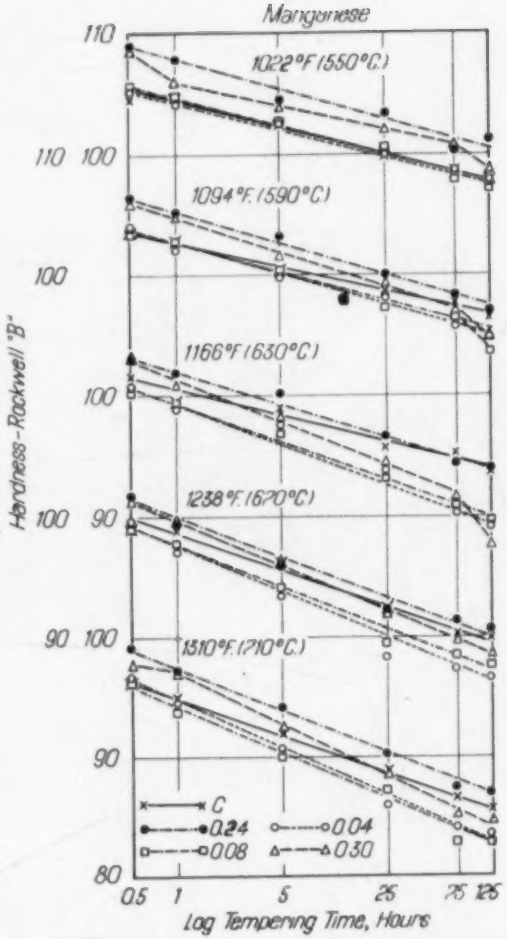

Fig. 3B—Semilogarithmic Plot Showing Relation Between Hardness and Time of Tempering at 550, 590, 630, 670 and 710 Degrees Cent. for the Manganese Steel.

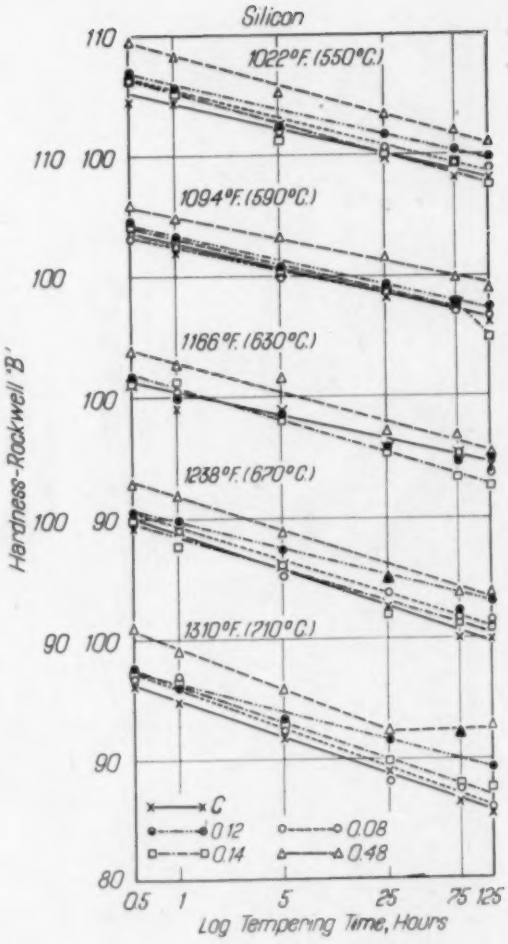

Fig. 3C—Semilogarithmic Plot Showing Relation Between Hardness and Time of Tempering at 550, 590, 630, 670 and 710 Degrees Cent. for the Silicon Steel.

obtained for the copper steels at this temperature after 75 and 125 hours renders it impossible to accurately determine the true hardness-time curve. Particularly noteworthy is the switch in position of the curves representing the behavior of the nickel and manganese alloys.

It has been pointed out previously (1), (5) that an approximate linear relationship exists between hardness and log tempering time with commercial hypereutectoid carbon steels when considered for times of tempering in excess of ½ hour. This type of plot is presented in Fig. 2 for the high alloy steels already discussed, in the study of Fig. 1, and it may be noted that general linearity obtains for all the alloys for both tempering temperatures. Certain peculiarities however may be noted. At 550 degrees Cent. (1020 degrees Fahr.) the nickel alloy fails to soften as profoundly at 75 and 125 hours as would be inferred from its behavior up to 25 hours tempering. The drop in hardness of the aluminum alloy has been explained on the basis of graphitization. At 710 degrees Cent. (1310 degrees Fahr.) the silicon and copper alloys show marked irregularity in softening behavior after 75 and 125 hours at temperature.

The displacement of the curves relative to the ordinate and the variation in slopes will be discussed in a later section.

In Figs. 3 and 4 have been assembled the semi-log plots of all steels except those to which aluminum was added. Thus in Fig. 3 we have, along with data illustrating the reaction to softening of the plain carbon steel, with respect to both time and temperature, similar data showing the effects of the so-called impurities found in quantity (except tin) in all commercial steels. The two carbon steels react alike (Fig. 3A) except for a slight difference found on tempering at 590 and 630 degrees Cent. (1095 and 1165 degrees Fahr.). The behavior of the sulphur and tin alloys indicates only minor differences from the carbon steels (Fig. 3A).

Considering then the manganese series (Fig. 3B), the resistance to softening is observed to be a function of the manganese content, but it should be noted that the phosphorus-bearing steel (No. 76) with 0.24 per cent manganese and 0.031 per cent phosphorus now classed as a manganese steel due to the inadvertent addition of this element, has the greatest hardness under any given treatment.

Similarly, resistance to softening is a function of silicon content (Fig. 3C) and the peculiar behavior of the high silicon alloy at 710 degrees Cent. (1310 degrees Fahr.) has already received comment.

In Figs. 4A, 4B, and 4C is illustrated the manner in which

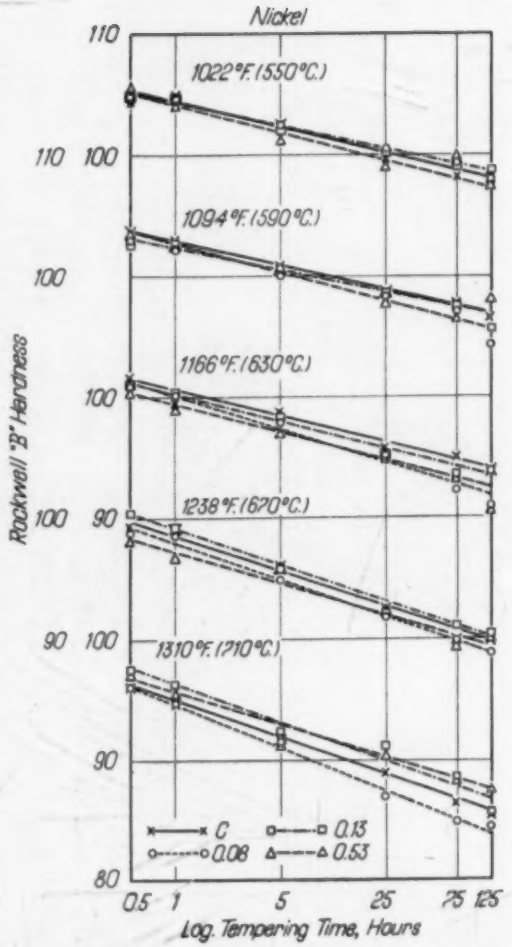

Fig. 4A—Semilogarithmic Plot Showing Relation Between Hardness and Time of Tempering at 550, 590, 630, 670 and 710 Degrees Cent. for the Nickel Steel.

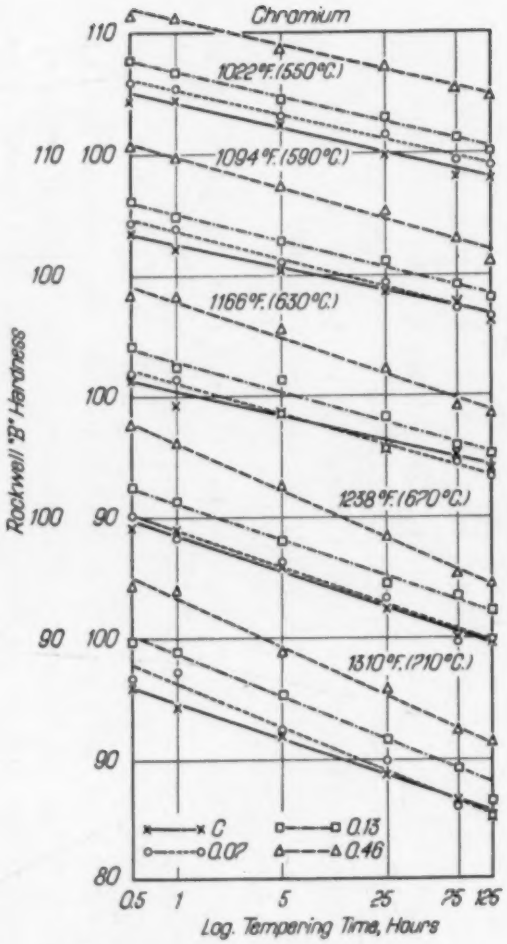

Fig. 4B—Semilogarithmic Plot Showing Relation Between Hardness and Time of Tempering at 550, 590, 630, 670 and 710 Degrees Cent. for the Chromium Steel.

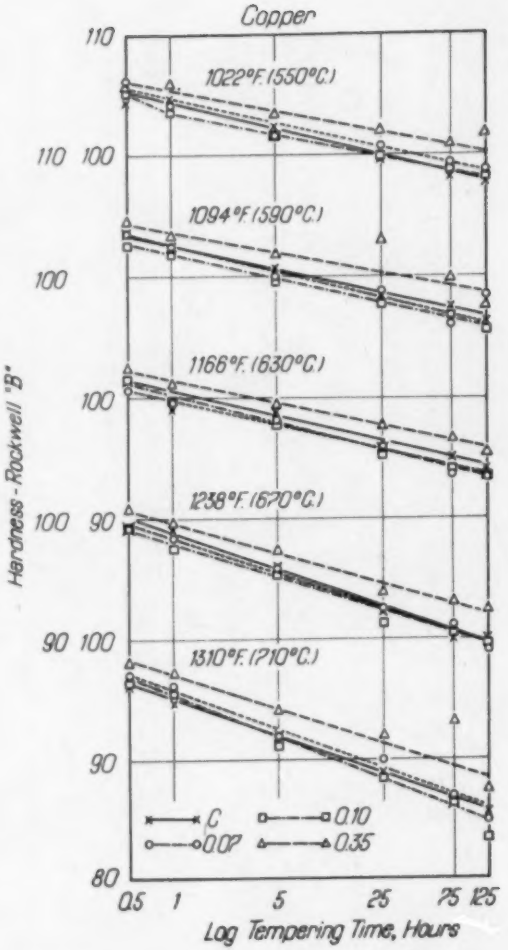

Fig. 4C—Semilogarithmic Plot Showing Relation Between Hardness and Time of Tempering at 550, 590, 630, 670 and 710 Degrees Cent. for the Copper Steel.

nickel, chromium and copper steels react to tempering. The nickel alloys are very similar to the plain carbon steels, but chromium exerts an effective resistance to softening (Fig. 4B) greater than that of any of the other alloying elements studied. Copper as an alloying

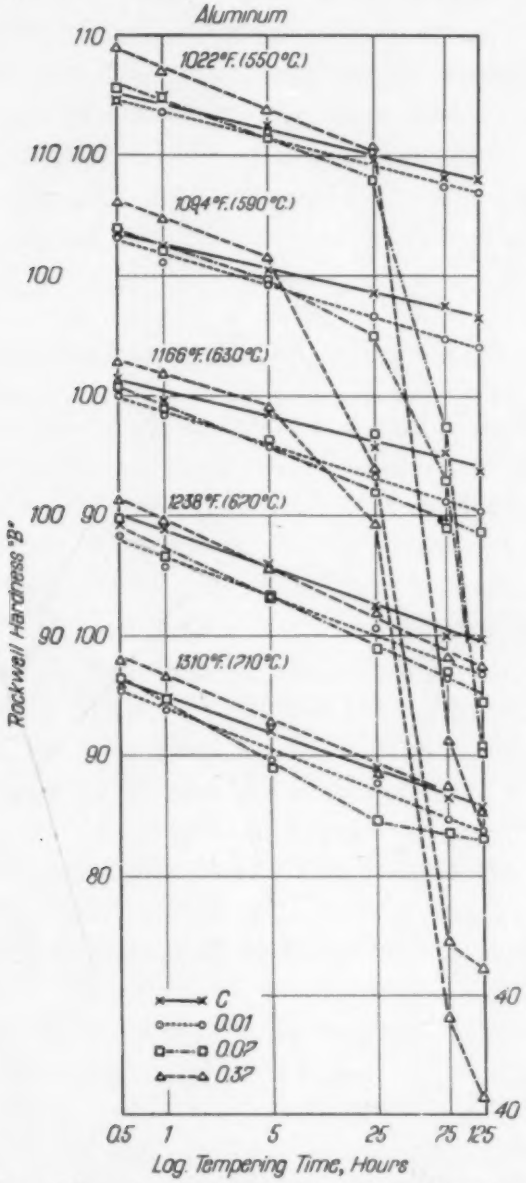

Fig. 5—Semilogarithmic Plot Showing Relation Between Hardness and Time of Tempering at 550, 590, 630, 670, and 710 Degrees Cent. for the Aluminum Steels.

element appears to result in an effect intermediate between that of nickel and chromium.

A study of the correlation between softening and time at tem-

perature for the aluminum alloys (Fig. 5) shows characteristics different from those already described. In the early stages of tempering all these steels exhibit the linearity previously noticed. However, when tempering is conducted at 550 and 590 degrees Cent. (1020 and 1095 degrees Fahr.) the alloy containing 0.07 per cent aluminum begins to show a rapid fall in hardness after 25 hours at temperature, whereas for the alloy with 0.37 per cent aluminum this characteristic is evident after 25 hours at 550 Cent. (1020 degrees Fahr. and after 5 hours treatment at 590 and 630 degrees Cent. (1095 and 1165 degrees Fahr.). This deviation from the semi-logarithmic linearity is dependent on graphitization and the phenomenon will be discussed fully in a later paper.

Analysis of Experimental Data

Since the basic alloys have been prepared so as to contain relatively small amounts of the elements commonly found in commercial carbon steels, it can be expected that relatively small differences in reaction to heat treatment will be observed in these studies. However, a consideration of the significance of the plots discussed, indicates that two principal factors are modified by the presence of a particular element. Thus it has been shown that chromium raises markedly the hardness level for the tempered alloy, at all temperatures studied. An indication of the magnitude of this effect can be indicated by some arbitrary intercept on the hardness ordinate. Since the Brinell hardness data represents a more fundamental measure of the hardness of an alloy, all recorded Rockwell values have been converted to the Brinell form for purposes of analysis. The significance of this procedure is more important when considering the second factor, discussed later.

Clearly zero time cannot be selected for comparison of intercepts since the alloys are initially all martensitic with a hardness of about 65 Rockwell C or 700 Brinell.

The simple equation to the straight line semi-log plots may be written in the form

$$B = a \log t + C$$

where B is Brinell hardness, t is time in hours, a is the slope of the line, and c is the hardness value where log t = O and consequently where t, or time of tempering, is 1 hour. For simplicity the intercept at this time has been selected for purposes of analysis.

The second principal factor which differentiates between the effect of the various alloying elements on reaction to tempering is the rate of softening at any given time or after any given hardness value has been attained.

In Fig. 6 all these values of the intercept C are shown plotted in seven charts, for carbon, sulphur and tin, and for each of the six other elements under consideration, while the eighth chart shows the data for the steels containing the maximum amount of the six elements charted separately.

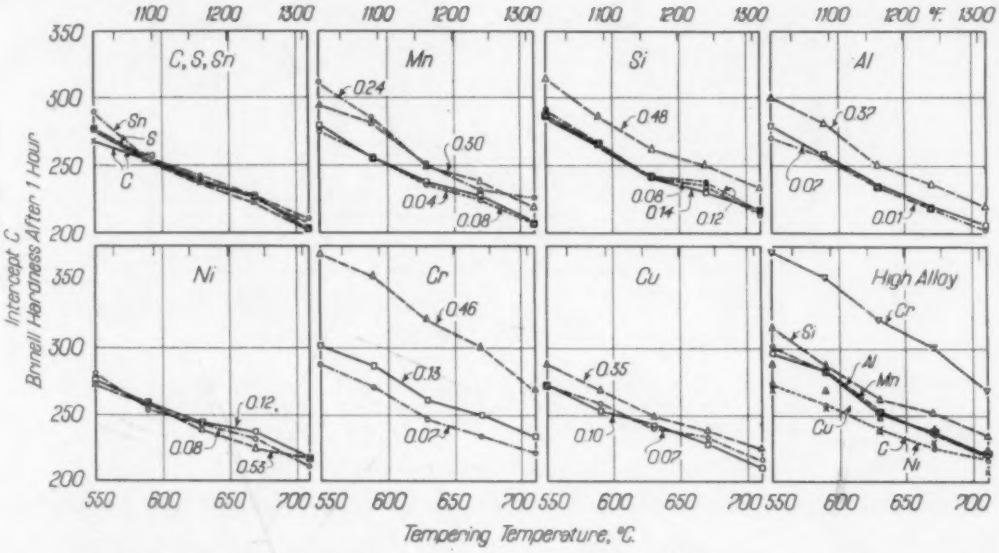

Fig. 6—Effect of Temperature on Intercept C (Brinell Hardness After Tempering for 1 Hour) for all Steels.

The intercepts C for the nickel, sulphur and tin steels, as well as for the steels containing the lowest amount of the other alloying elements, are observed to be similar to the intercept for the carbon steels. This of course means that for 1-hour treatment at a given temperature these alloys softened to the same extent, approximately at all temperatures ranging from 550 to 710 degrees Cent. (1020 to 1310 degrees Fahr.). However, larger quantities of manganese, silicon, aluminum, and copper increase the resistance to softening to some extent. Thus in amounts up to about ½ per cent these elements will cause a hypereutectoid steel after a temper of 1 hour to show a hardness that is 10 to 30 Brinell hardness units greater than a carbon steel after a similar heat treatment. When, however, the alloying element is chromium, the difference is quite marked, 0.5 per cent chromium increasing the hardness by 70-100 units. The relative

behavior of these higher alloy steels is clearly illustrated by the chart at the lower right-hand corner of Fig. 6.

These observations are further emphasized by arrangement of the hardness data in the form, shown in Fig. 7. Here the added elements are listed along the abscissa in decreasing order of effective

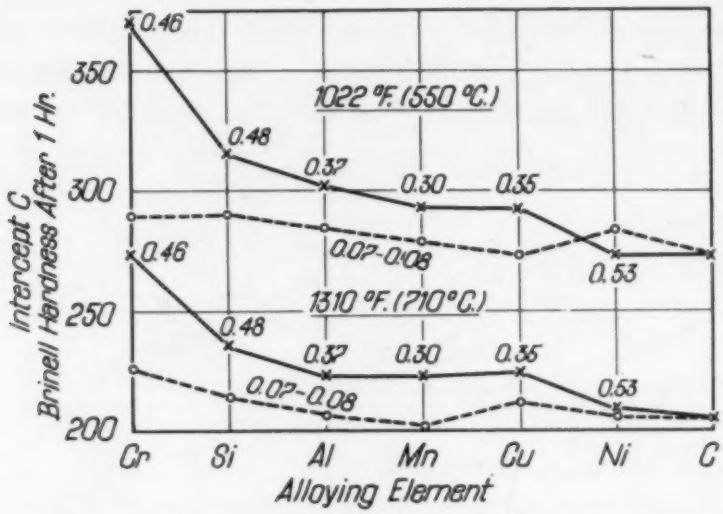

Fig. 7—Effect of Low and High Amounts of Alloy on Intercept C (Brinell Hardness After Tempering for 1 Hour) at 550 and 710 Degrees Cent.

resistance to softening at the lowest and highest tempering temperature studied. The solid lines join the hardness values plotted for the steels with the highest amount of alloy, while the steels containing an approximate constant amount, 0.07-0.08 per cent, are connected by the broken lines. It is quite evident that ½ per cent chromium is much more effective than a similar quantity of silicon while an even greater percentage of nickel exerted little effect. It is interesting to note that small quantities of the alloying elements have no marked effect on the steels tempered at 550 or 710 degrees Cent. (1020 or 1310 degrees Fahr.).

Attention is now directed to an analysis of the second stated factor, namely, the effects of the elements on the rate of softening under given conditions. This information can be obtained by calculation of a series of values for the slope of the tangent as this changes with time along the Brinell hardness-time curves. Clearly these data may then be analyzed in their relation either to elapsed time of tempering or to certain specific hardness values. It is believed that the effectiveness of an alloy in its modification of rate of tempering is

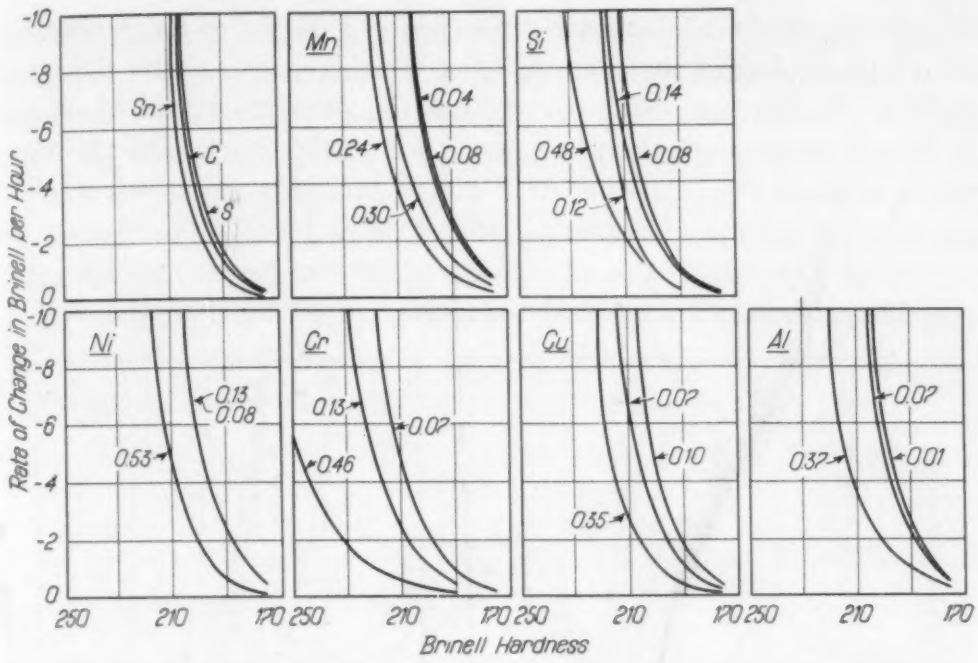

Fig. 8—Chart Showing Rate of Change of Softening as a Function of Hardness for all Steels when Tempered at 710 Degrees Cent.

better indicated by a correlation with hardness, as will be discussed in connection with Figs. 8, 9, and 10.

The data for these curves were obtained in the following manner, using Brinell conversions instead of Rockwell B recorded data, throughout. Since the equation

$$B = a \log_{10} t + C \qquad (1)$$

is the equation of the hardness-times curves (type Fig. 1) as well as for the straight line obtained for the semi-log plots (type Fig. 2), its first derivative will be the slope of the hardness-time curve at any given hardness. Changing the logarithm to the base e equation (1) becomes

$$B = 0.434\, a \log_e t + C \qquad (2)$$

and the first derivation of this expression is

$$\frac{dB}{dt} = \frac{0.434\, a}{t} \qquad (3)$$

Thus having obtained the a values (slope) for the hardness-log time plots of each of the alloys at the various tempering temperatures, a simple calculation provides the necessary data to complete the plots expressed in Figs. 8, 9, and 10.

In Fig. 8 all curves relate to calculations made from the tempering studies made at 710 degrees Cent. (1310 degrees Fahr.) where

the various steels exhibit least difference in reaction to tempering. It is well to emphasize that the ordinate, which represents the change in slope of the hardness-time curves, has the significant rate of change in Brinell hardness per hour, as expressed on the chart. Thus all these curves indicate the following well-known facts for any given steel:

(1) The rate of softening decreases with fall in hardness, and

(2) The rate of this change also decreases as the metal softens.

The carbon, sulphur, and tin steels are grouped in the first of

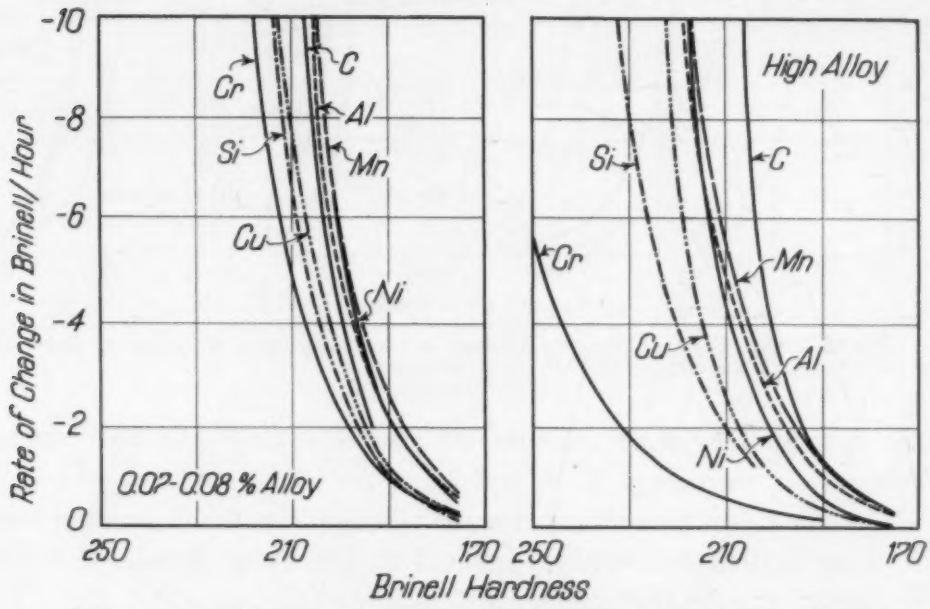

Fig. 9—Chart Showing Comparison of Effects of 0.07 to 0.08 Per Cent, and Approximately ½ Per Cent Added Element on the Rate of Change of Softening of Alloys, as a Function of Hardness When Tempered at 710 Degrees Cent.

the seven graphs, while the remaining graphs include one of each of the six other alloying elements. It may be noted that all the elements exert some effect on the position of the curves although the locations of the steels containing the lowest amount of alloying element are not very different from that of the carbon steels. In practically all cases, as the amount of alloy increases, the curve is shifted to the left. This behavior is particularly marked with the chromium alloys. The interpretation of these observations is that at a given hardness the rate of softening is decreased by increase in alloy content, and this resistance to tempering is most strongly exhibited by the presence of chromium.

The apparent exception to the above generalization may be noted in the manganese steels. Thus the curve for the 0.24 per cent manganese steel lies to the left of that for the 0.30 per cent manganese

steels, indicating superior resistance to softening. This difference in behavior however is probably indicative of the resistance to tempering imparted by the addition of 0.031 per cent phosphorus to the 0.24 per cent manganese alloy. Some abnormalities can be noted in the silicon and in the copper steels.

Some of the curves in Fig. 8 have been consolidated into two graphs shown in Fig. 9 where a much clearer correlation of element effect is obtained. Thus even when the amount of alloying element is small (0.07-0.08 per cent) some classification of the alloys may be made. The aluminum, manganese, and nickel steels appear to have

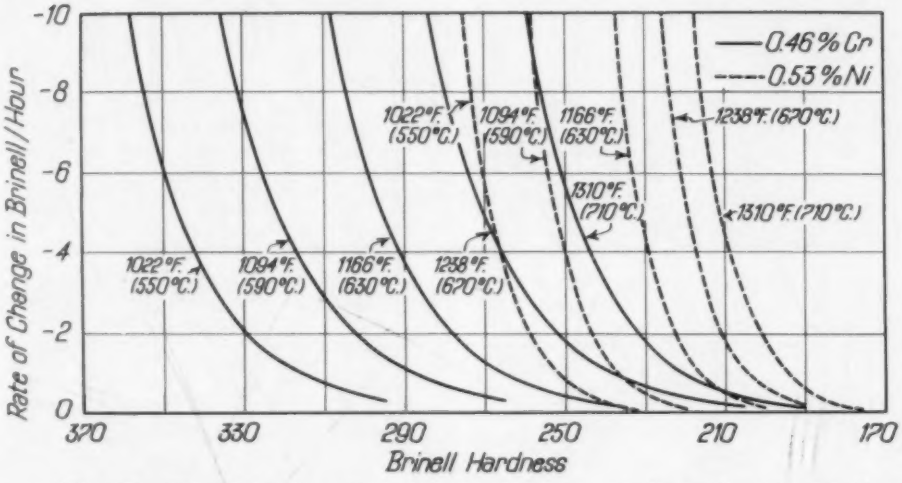

Fig. 10—Chart Showing Comparison of Effects of Approximately ½ Per Cent Chromium and Nickel on the Rate of Change of Softening as a Function of Hardness for all Tempering Temperatures Investigated.

a slightly greater rate of softening than the carbon steel, but the copper, silicon and chromium are increasingly effective as compared with the carbon steel, in their resistance to tempering or softening.

It is interesting to note that in the high alloy steels (containing about ½ per cent added element) the arrangement of the curves is the same as for the low alloy steels. However, the degree of separation is much greater and the plain carbon steel now exhibits least resistance to softening by tempering. Aluminum, manganese, and nickel react quite similarly, while chromium, silicon and copper produce lower rates of softening at any given hardness than the other elements. It is quite evident that chromium reduces the rate much more effectively than either silicon or copper.

In order to illustrate the effect of change in temperature on the rate of softening with respect to hardness two steels exhibiting widely different rates, at a given temperature, namely, 0.53 per cent nickel

and 0.46 per cent chromium alloys, have been compared. Incidentally the curves representing the nickel steel are not markedly different from those for the plain carbon steel. Isothermal curves for these steels are shown in Fig. 10 where it is manifest that at a given hardness, the rate of softening of both steels is increased as the tempering temperature is raised. The important point, however, is revealed by the grouping of the alloys with respect to the Brinell hardness co-ordinate. Thus in making comparison for a common rate of soft-

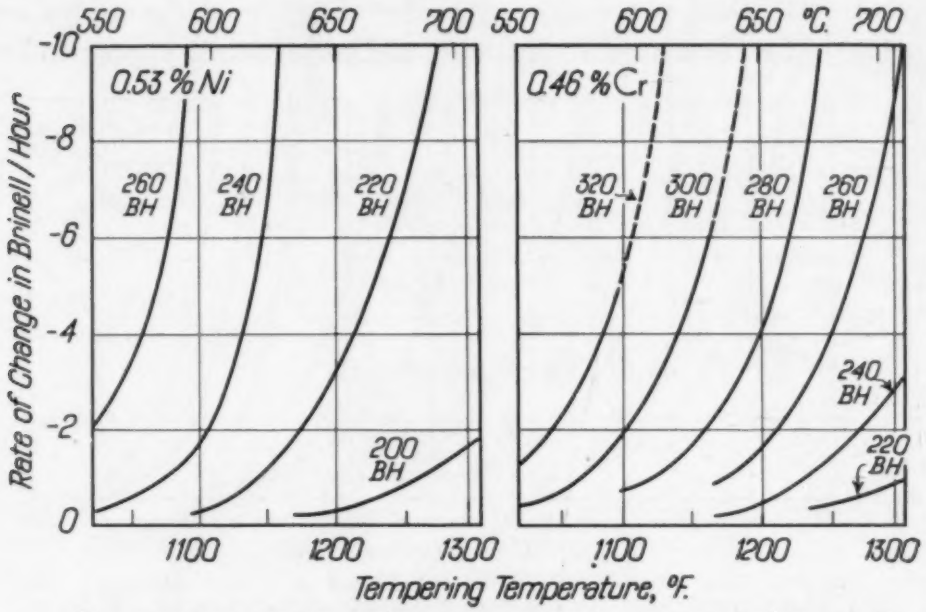

Fig. 11—Chart Showing Comparison of Effects of Approximately ½ Per Cent Nickel and Chromium on the Rate of Change of Softening as a Function of Temperature at Selected Hardness Values.

ening of 10 Brinell hardness units per hour at 550 degrees Cent. (1020 degrees Fahr.), the nickel alloy shows this softening rate at 275 Brinell where under similar conditions the chromium alloy exhibits a similar softening rate at about 360 Brinell. On the other hand, when both have been given the time necessary to attain a common hardness, say 275 Brinell, while the nickel steel is still dropping in hardness at a rate of 10 units per hour the chromium alloy is decreasing in hardness at a rate much less than 1 unit per hour.

Probably this factor is better revealed by the plot prepared in Fig. 11, where the rate of softening is plotted against tempering temperature. It is quite evident from these curves that at a given hardness such as 240 Brinell, the rate of softening of the nickel steel increases much more rapidly with temperature than it does in the chromium steel.

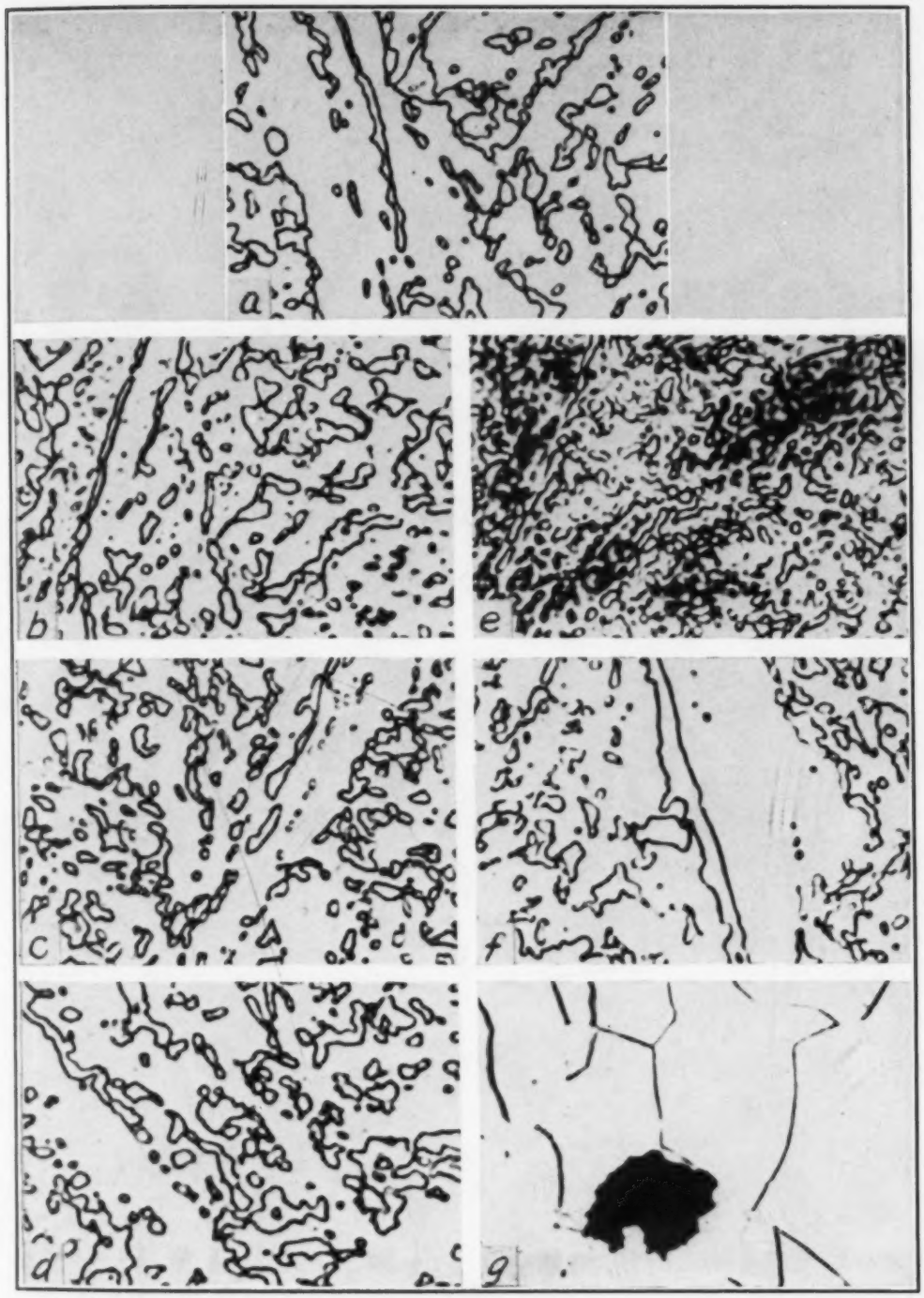

Fig. 12—Photomicrographs of Carbon and High Alloy Steels (Approximately ½ Per Cent Added Element) Tempered 125 Hours at 550 Degrees Cent. a.—Carbon. b.—0.30 Mn. c.—0.48 Si. d.—0.53 Ni. e.—0.46 Cr. f.—0.35 Cu. g.—0.37 Al. × 2000. Picric Acid Etch for a to f, Nitric Acid Etch for g.

METALLOGRAPHY

It is of importance to study the relation of the changes in hardness, as already discussed in the paper, with the changes in micro-

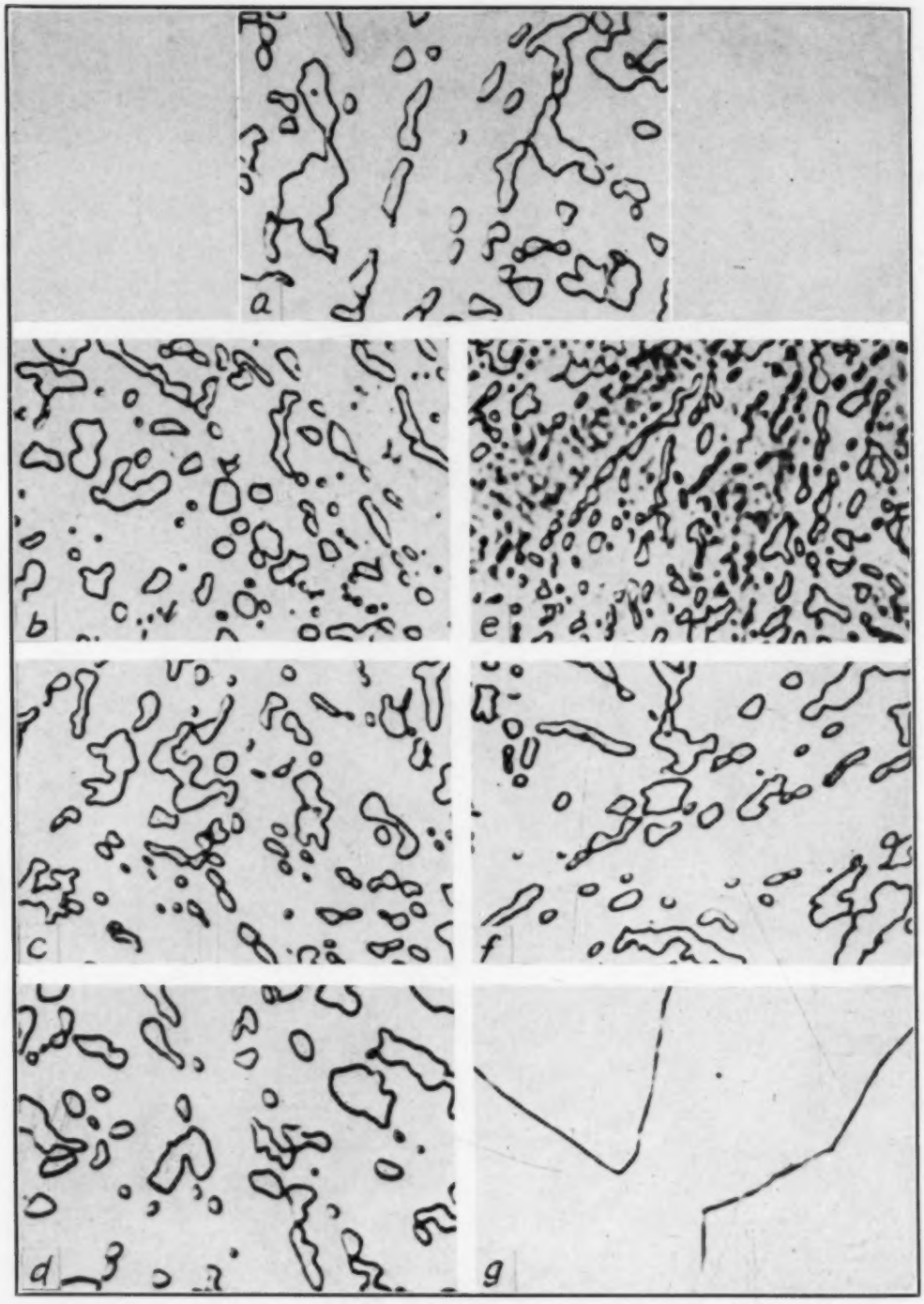

Fig. 13—Photomicrographs of Carbon and High Alloy Steels (Approximately ½ Per Cent Added Element) Tempered 125 Hours at 630 Degrees Cent. a.—Carbon. b.—0.30 Mn. c.—0.48 Si. d.—0.53 Ni. e.—0.46 Cr. f.—0.35 Cu. g.—0.37 Al. × 2000. Picric Acid Etch for a to f, Nitric Acid Etch for g.

structure and the progress in the spheroidization of the steels. Many of the structures of the tempered alloys have been examined and

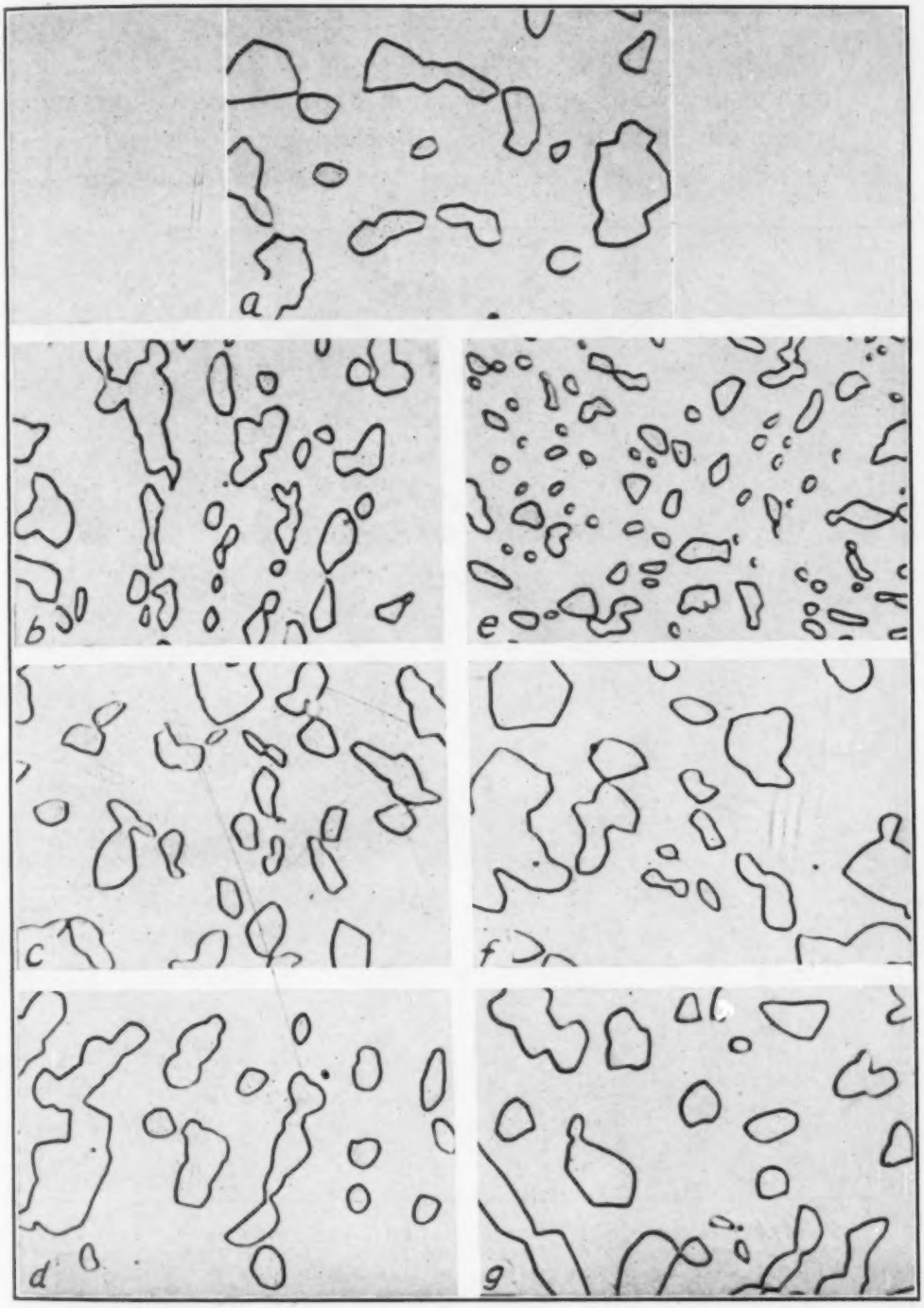

Fig. 14—Photomicrographs of Carbon and High Alloy Steels (Approximately ½ Per Cent Added Element) Tempered 125 Hours at 710 Degrees Cent. a.—Carbon. b.—0.30 Mn. c.—0.48 Si. d.—0.53 Ni. e.—0.46 Cr. f.—0.35 Cu. g.—0.37 Al × 2000. Picric Acid Etch for All Steels.

typical photomicrographs have been selected for inclusion in this report in order to illustrate:

1. The effect of change in temperature of tempering (550 to 710 degrees Cent.) for a constant time of 125 hours on the degree of spheroidization of the steels containing the maximum amount of each of the alloying elements.

2. The effect of time at one selected temperature (710 degrees Cent.) on the progress of spheroidization of the high nickel and high chromium steels.

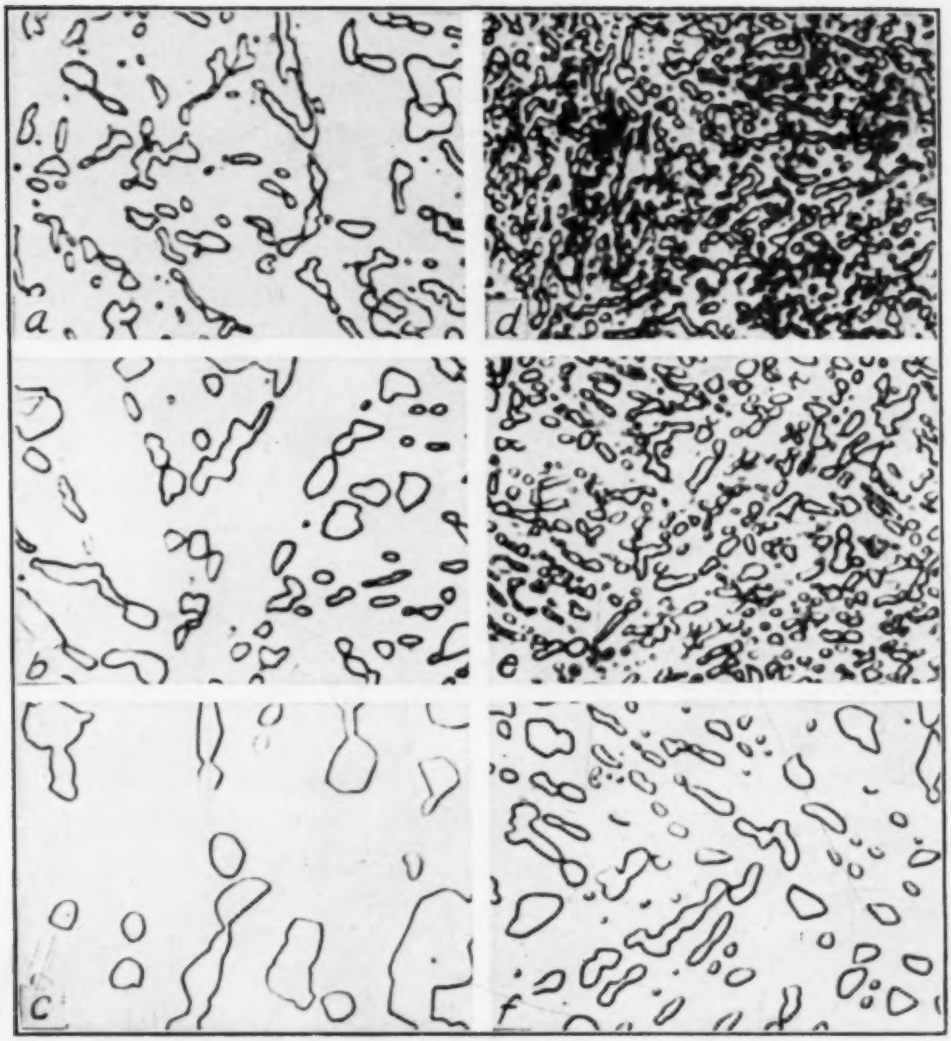

Fig. 15—Photomicrographs of 0.53 Per Cent Nickel and 0.46 Per Cent Chromium Steels, Tempered at 710 Degrees Cent. for 1, 5, and 125 Hours. 0.53 Per Cent Ni Steel a.—1 Hour. b.—5 Hours. c.—125 Hours. 0.46 Per Cent Cr Steel d.—1 Hour. e.—5 Hours. f.—125 Hours. Picric Acid Etch. × 2000.

The structures obtained at 550 degrees Cent. (1020 degrees Fahr.) after 125 hours for the high alloy steels are reproduced in Fig. 12. Except for the chromium and aluminum steels the results are quite

similar to that of the plain carbon steel. The carbides in the chromium steel are much smaller than those in the other alloys, while no carbides exist in the aluminum steel, since they have been completely decomposed into graphite and free ferrite. When the tempering temperature is raised to 630 degrees Cent. (1165 degrees Fahr.) (Fig. 13) large carbides are formed in all steels, but carbide growth appears to have occurred to a slightly greater degree in the nickel and plain carbon steels. The chromium steel continues to show the smallest carbides while complete graphitization still persists in the aluminum alloy.

In Fig. 14 (710 degrees Cent.) (1310 degrees Fahr.) it is evident that the carbon, nickel and copper steels contain the largest carbides while the least degree of spheroidization still persists in the chromium steel. The aluminum is free from graphitization and has spheroidized to a degree comparable with the alloys containing silicon and manganese.

The effect of time at 710 degrees Cent. (1310 degrees Fahr.) on the high nickel and chromium steels is illustrated in Fig. 15.

General Conclusions

The following conclusions may be drawn concerning the hardness and microstructure of pure 1.1 per cent carbon steels to which have been added 0.5 per cent or less of a third element, when the hardened steels are tempered in the temperature range 550 to 710 degrees Cent. (1020 to 1310 degrees Fahr.) for time intervals of 30 minutes up to 125 hours.

1. Approximate linear relationship exists between Rockwell B, or Brinell hardness and logarithm of the tempering time from 30 minutes to 125 hours for all alloys at all temperatures investigated, so long as graphitization does not occur. With the highest aluminum it has been recorded that graphitization may be complete at 550 to 630 degrees Cent. (1020 to 1165 degrees Fahr.) after 125 hours. In the initial stages of tempering the reaction is complex involving both the release of strain and the decomposition of martensite. The tempering reaction from 30 minutes onwards is essentially a process of carbide spheroidization.

2. In the alloys containing approximately 0.5 per cent added element, data obtained at the end of the short tempering period of one hour at all tempering temperatures, indicate that manganese, silicon,

aluminum and copper show a hardness number from 10 to 30 Brinell units greater than that of the plain carbon steel. Nickel shows no apparent effect, whereas chromium exhibits a resistance to softening which is profoundly different from that of any of the other alloying elements investigated. Thus after 1 hour at 550 degrees Cent. (1020 degrees Fahr.) the chromium steel is about 100 Brinell units harder than the carbon steel and even after 1 hour at 710 degrees Cent. (1310 degrees Fahr.) this difference is 70 Brinell units.

3. For the alloys containing less than 0.15 per cent added element, the data obtained after 1-hour treatment at each of the five tempering temperatures demonstrate that with the exception of chromium little resistance to softening is obtained.

4. In an effort to provide an analysis of the relative effectiveness of the various alloying elements on resistance to softening, curves have been presented which show the variation in rate of softening (expressed as rate of change in Brinell hardness per hour) at constant temperature (710 degrees Cent.), with change in hardness. This analysis showed the relatively minor effects of added element up to 0.08 per cent, but it clearly revealed that for approximately 0.5 per cent of element present, manganese, nickel, and aluminum cause only a small increase in resistance to softening while copper, silicon and chromium show increasingly marked effect, in the order listed.

5. Similarly, data have been derived to permit presentation of curves to illustrate the effect of temperature on the variation in softening rate, with change in hardness on both the chromium and nickel alloys containing approximately 0.5 per cent of these elements. At all temperatures investigated the relative rate of softening at any selected Brinell hardness was very much greater for the nickel than for the chromium steel. Indeed the conditions obtaining with the nickel alloy were not very different from those for the plain carbon steel.

6. Plots for the variation in rates of softening at selected hardness values with increase in tempering temperature, for the high nickel and chromium alloys further illustrate and emphasize the difference in behavior of these two elements.

7. Selected photomicrographs obtained from several samples of the tempered alloys have been included to illustrate the correlation between change in hardness and the degree of carbide spheroidiza-

tion of the steels. The microstructure of a completely graphitized aluminum alloy has also been included.

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3. C. R. Austin and M. C. Fetzer, "Reactions to Annealing Above the Eutectoid Temperature of Quenched Hypereutectoid Steels," TRANSACTIONS, American Society for Metals, Vol. 27, 1939, p. 18.
4. R. D. Steigerwalt, "Austenitic Grain Size of Pure Low-Alloy Steels." Unpublished Senior Thesis, The Pennsylvania State College, 1939.
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DISCUSSION

S. W. POOLE:[1] The paper just presented is of fundamental importance in regard to the effects of alloy elements in tempering. From the technique adopted it is apparent that important data could be arrived at concerning the specific effects in tempering of the commercially important alloying elements.

If further work is to be done along these lines, it would be of interest to find out something concerning the effect of nitrogen, which has very definite effects in inhibiting softening during tempering. Nitrogen could be added to the electrolytic iron base melts as calcium cyanamide or be possibly introduced in the gaseous form. The specific effects of molybdenum, which is used in several important alloy steels in amounts less than ½ per cent, might also be worth investigating.

J. T. MACKENZIE, JR.:[2] I was interested in noting that only one alloy, namely, that which contained aluminum, graphitized within the 125 hours of tempering employed by the authors.

In this connection, a paper presented before the American Society for Metals in 1937 by Wells showed that high purity iron-carbon alloys, containing about one per cent carbon, graphitized to some extent within 150 hours of tempering at 700 degrees Cent.

It would be interesting to know whether the alloys studied by the authors would graphitize if held at their tempering temperatures for longer periods of time (150 to 200 hours) than those employed by them in this investigation.

Authors' Reply

The authors appreciate the comments of Messrs. Poole and MacKenzie.

The researches of Wells on high purity iron-carbon alloys, containing

[1]Metallurgical assistant, Republic Steel Corp., Canton, O.
[2]U. S. Steel Corp., Research Laboratory, Kearny, N. J.

about 1 per cent carbon, provided data on graphitization at temperatures above the critical, while the present investigation considers only carbide instability on long tempering below the critical. Furthermore, while profound graphitization was found only in the aluminum steels, under the conditions of heat treatment outlined in the paper, the authors expect to develop the subject of carbide instability in the other alloys in a future paper.

As Mr. Poole points out it has been the endeavor of the authors to develop quantitative data of fundamental importance. The role of nitrogen as an inhibitor to softening has not been considered, nor has a molybdenum alloy been investigated. In this preliminary survey selection of elements commonly found in small quantities in plain carbon steels was made. The effects of several other elements still remain to be investigated.

THE EFFECT OF IMPURITIES ON SOME HIGH TEMPERATURE PROPERTIES OF COPPER

By E. R. Parker

Abstract

Stress versus time-for-failure tests were made on an oxygen-free high conductivity copper at 200 degrees Cent. and on an oxygen-free copper containing 0.054 per cent of silver at 250 degrees and 200 degrees Cent. The test data show that samples of both coppers water quenched from 850 degrees Cent. (1560 degrees Fahr.) are much more susceptible to intergranular failure under sustained loads at high temperatures than are furnace cooled samples. The difference is explained as being due to a difference in concentration of impurities in the grain boundary material resulting from the variation in cooling rate.

The recrystallization of cold-rolled tough pitch copper, tough pitch copper deoxidized in hydrogen, oxygen-free high conductivity copper, and an oxygen-free copper containing silver were studied. It was suggested that the low recrystallization temperature of tough pitch copper is at least partly due to the oxide particles, which cause more than average strain in the surrounding metal during rolling. The cold-rolled oxygen-free copper containing silver was found to be precipitation hardening. The high recrystallization temperature of this material was attributed to the presence of the precipitated silver-rich phase.

Introduction

A GREAT deal of work has been done concerning the effect of impurities on the recrystallization temperature of copper. Caeser and Gerner showed as early as 1916 (1)[1] that 0.10 per cent of silver added to copper raises the recrystallization temperatures 100 degrees Cent. Other workers have shown that as little as 0.02 per cent of silver has a marked effect on the recrystallization temperature (2). It is well known that small quantities of other elements such as antimony, arsenic, etc., similarly affect the recrystallization temper-

[1]The figures appearing in parentheses refer to the bibliography appended to this paper.

A paper presented before the Twenty-second Annual Convention of the Society held in Cleveland, October 21 to 25, 1940. The author is associated with the research laboratory, General Electric Co., Schenectady, N. Y. Manuscript received July 17, 1940.

ature. Caeser and Gerner likewise noted that the presence of cuprous oxide in copper caused a lowering of the recrystallization temperature.

The effect of small quantities of silver or other elements on the temperature required to produce an intercrystalline fracture (in a given time) in stressed copper was recognized some time ago. In 1935, T. S. Fuller and L. L. Wyman* found that tough pitch copper when heated to 165 degrees Cent. and subjected to a high static tensile load would fail with an intercrystalline fracture in 20 hours. Similar copper containing 0.03 per cent of silver had to be heated under stress for 140 hours at 300 degrees Cent. to produce an intercrystalline failure.

Only one atom of silver to 5000 atoms of copper can produce this great change in properties! Can the silver be so effective if it is uniformly distributed, or is this large effect the result of a concentration of silver in certain localities? Intercrystalline failures reflect primarily the strength of the grain boundary material; so it seems possible that the concentration of silver may be greater in the grain boundaries than in the grains. If such is the case, the large effects resulting from such a small amount of silver could be more easily accounted for. The copper-silver phase diagram does not exclude the possibility of silver concentrating in grain boundaries. The solubility of silver in solid copper drops rapidly from a maximum of 8 per cent at 780 degrees Cent. (1435 degrees Fahr.) to practically zero at 200 degrees Cent. (390 degrees Fahr.). There is no visible evidence of segregation in copper containing a small amount of silver, but nevertheless certain experimental evidence seems to favor this viewpoint.

Intercrystalline failures in copper result from specific combinations of stress and temperature. A test which produces intercrystalline fractures can be used as a measure of the cohesion between grains and should therefore be a sensitive indicator of changes in the nature of the grain boundary material. The "sustained-load rupture test" is suitable for determining the high temperature strength of materials; so the experimental data presented herein are mainly of this type.

Experimental Procedure

The materials used for the experiments were commercial oxygen-free high conductivity copper and an oxygen-free high conductivity

*Both of the General Electric Company.

copper containing 0.054 per cent of silver prepared by S. Rolle of the Scomet Engineering Company. Some work was also done on commercial tough pitch copper containing about 0.035 per cent of oxygen. The qualitative spectographic analyses of these coppers are reported in Table I along with the results of a very careful chemical analysis of the silver.

Table I
Spectrographic Analysis of Coppers

Element	Tough Pitch	Oxygen-Free High Conductivity	Oxygen-Free Containing Ag
Ag	Nil (0.0010%)*	Trace (0.0020%)*	Low (0.054%)*
Al	Trace	Low	Nil
As	Nil	Nil	Nil
B	Nil	Nil	Nil
Ba	Nil	Nil	Nil
Bi	Nil	Nil	Nil
Ca	Trace	Trace	Nil
Cn	Nil	Nil	Nil
Fe	Trace	Trace	Trace
Mn	Nil	Nil	Nil
Ni	Nil	Nil	Nil
Pb	Nil	Nil	Nil
Sb	Nil	Nil	Nil
Si	Trace	Trace	Trace
Sn	Nil	Nil	Nil
Zn	Nil	Nil	Nil

*Chemical Analysis.

Recrystallization temperatures were determined for all three coppers on samples which had been cold rolled from 1 inch to 0.1 inch.

Rupture tests were conducted in air on the oxygen-free coppers at various elevated temperatures by subjecting test bars to various constant loads and measuring the time required for fracture. Elongation and reduction of area were measured after fracture, and the broken bars were examined microscopically. The test bars were machined from copper which had been cold swaged from 0.5 to 0.25 inch diameter. The samples were 2 inches long and threaded on each end with quarter-twenty threads. The center portions of the bars were reduced to 0.1596 inch for a 1-inch gage length. The samples were suspended in the hot zone of a furnace by long extension rods, and the loads were applied through simple levers. The temperature was automatically controlled within $\pm$ 1 degree Cent. and the temperature gradient in the furnace was less than 1 degree in 4 inches. The life of each bar was measured with an hour meter which was automatically tripped off when the bar broke.

The machined bars of the oxygen-free copper containing silver were heated in hydrogen at 850 degrees Cent. (1560 degrees Fahr.)

for 1 hour. Some of the bars were furnace cooled at approximately 90 degrees Cent. per hour and some were water quenched. All bars were carefully supported during heat treatment to protect them from bending. At 850 degrees Cent. (1560 degrees Fahr.) the solubility of silver in copper is high and the mobility of the atoms is great. At this temperature the silver tends to become uniformly distributed throughout the copper. If there is any tendency for the silver to concentrate in the grain boundaries, the slow cooling would favor the concentration. The distribution of silver in the water quenched samples would be very nearly the same as it was at the high temperature, i.e., a minimum of silver in the grain boundaries. The strength of the grain boundary material would depend upon the concentration of silver atoms; so, if the silver actually segregates, the grain

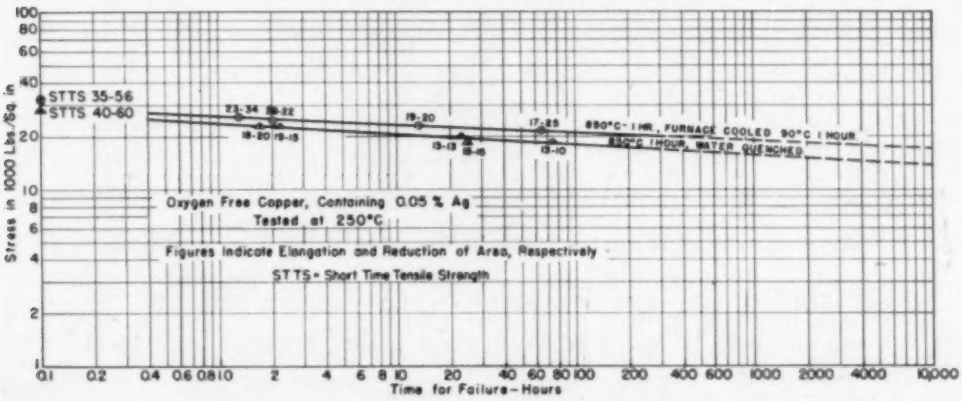
Stress in 1000 Lbs./Sq. In.
STTS 35-56
STTS 40-60
850°C - 1 HR., FURNACE COOLED 90°C / HOUR
850°C / HOUR, WATER QUENCHED
Oxygen Free Copper, Containing 0.05 % Ag
Tested at 250°C
Figures Indicate Elongation and Reduction of Area, Respectively
STTS = Short Time Tensile Strength
Time for Failure - Hours

Fig. 1—Stress vs. Time-for-Failure Data at 250 Degrees Cent. on Oxygen-Free Copper Containing Silver.

boundary material of the furnace cooled bars should be somewhat stronger than that of the water quenched copper. Results of sustained-load rupture tests at 250 and 200 degrees Cent., Figs. 1 and 2, are in accord with this interpretation.

There are several interesting characteristics brought out by these results. Tests at 250 degrees Cent. (480 degrees Fahr.) show that the water quenched bars are considerably weaker than the furnace cooled samples. The short time tensile strength is lower for the water quenched material, but the elongation and reduction of area are high. Both short time fractures were transcrystalline. The long time fractures were intercrystalline. The transition from transcrystalline to intercrystalline failure was gradual; so intermediate fractures occur partly through the grains and partly around them. It is interesting to note how the elongation and reduction of area decrease

as the fracture becomes more intercrystalline and assumes a "brittle" appearance. Microscopic examination of the failed bars revealed that the water quenched samples, which failed with much less elongation and reduction of area, were considerably more susceptible to intercrystalline failure than the furnace cooled bars. The stress vs. time-for-failure data obtained at 200 degrees Cent. (Fig. 2) yielded similar results.

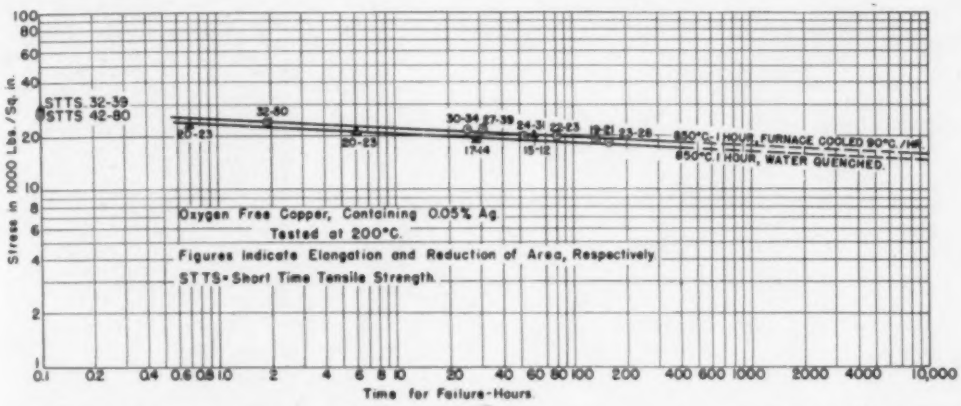
Stress in 1000 Lbs / Sq. in.
STTS 32-39
STTS 42-80
Oxygen Free Copper, Containing 0.05% Ag
Tested at 200°C.
Figures Indicate Elongation and Reduction of Area, Respectively
STTS = Short Time Tensile Strength
850°C-1 HOUR, FURNACE COOLED 50°C / HR.
850°C-1 HOUR, WATER QUENCHED
Time for Failure-Hours

Fig. 2—Stress vs. Time-for-Failure Data at 200 Degrees Cent. on Oxygen-Free Copper Containing Silver.

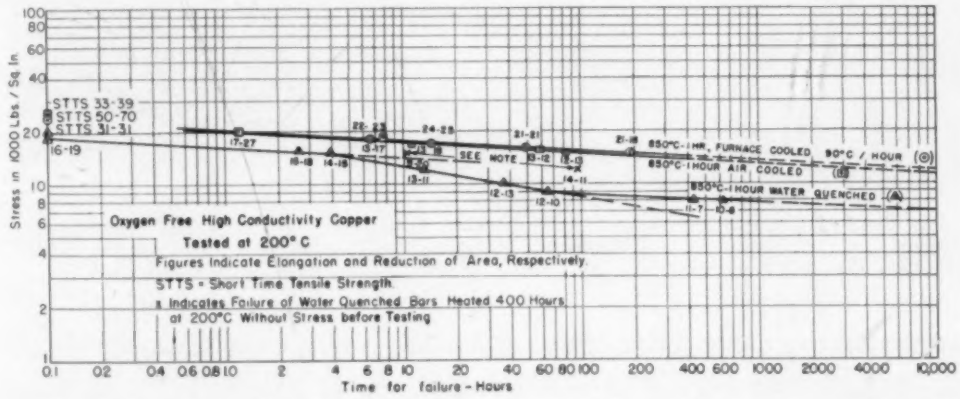
Stress in 1000 Lbs / Sq. In.
STTS 33-39
STTS 50-70
STTS 31-31
Oxygen Free High Conductivity Copper
Tested at 200° C
Figures Indicate Elongation and Reduction of Area, Respectively
STTS = Short Time Tensile Strength
x Indicates Failure of Water Quenched Bars Heated 400 Hours at 200°C Without Stress before Testing
850°C-1 HR., FURNACE COOLED 50°C / HOUR
850°C-1 HOUR AIR COOLED
850°C-1 HOUR WATER QUENCHED
Time for failure - Hours

Fig. 3—Stress vs. Time-for-Failure Data at 200 Degrees Cent. on Oxygen-Free High-Conductivity Copper.

These results indicate rather clearly that the strength of the grain boundary material in oxygen-free copper depends upon the heat treatment to which the copper has been subjected; so these experiments are in accord with the hypothesis suggesting a concentration of silver in the grain boundaries.

The oxygen-free high conductivity copper was heat treated exactly like the silver-bearing oxygen-free copper so that the effect of the silver could be evaluated. The grain size of the two coppers was

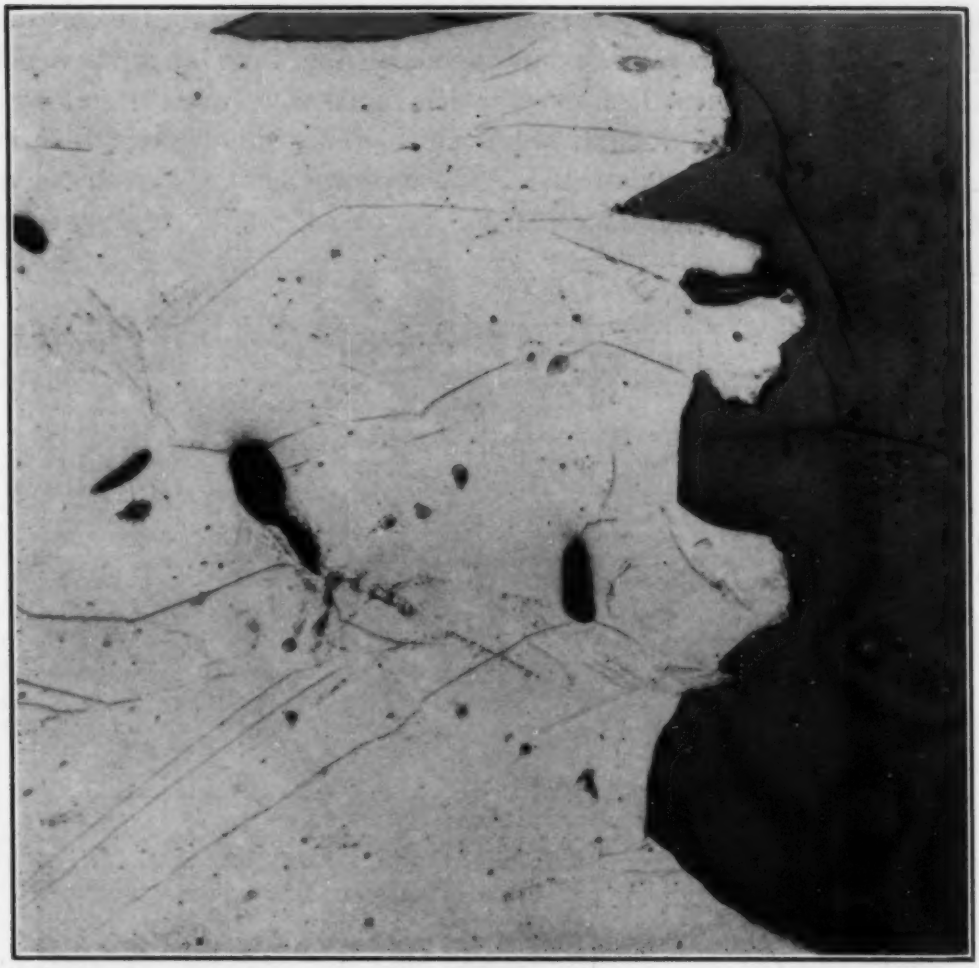

Fig. 4a—An Oxygen-Free High-Conductivity Copper. Heated 1 Hour in Hydrogen at 850 Degrees Cent., Furnace-Cooled 90 Degrees Cent. Per Hour. Tested in Air at 200 Degrees Cent. Stress 16,000 Pounds Per Square Inch; Life 48.4 Hours; Elongation 21 Per Cent; Reduction of Area 21 Per Cent. × 75.

essentially the same after heat treatment. The results obtained with the oxygen-free high conductivity copper at 200 degrees Cent. are shown in Fig. 3. The tremendous decrease in strength produced by water quenching was surprising. The strength of the grain boundary material in this copper is certainly dependent upon the cooling rate from 850 degrees Cent. (1560 degrees Fahr.) because the only difference in the history of the samples was the cooling rate from this high temperature. The stress which will produce failure in 100 hours is about 15,000 pounds per square inch for the furnace cooled material but less than 9000 pounds per square inch for the water quenched material, a decrease in strength of over 40 per cent! Fractures are shown in Figs. 4 and 5 of furnace cooled and water

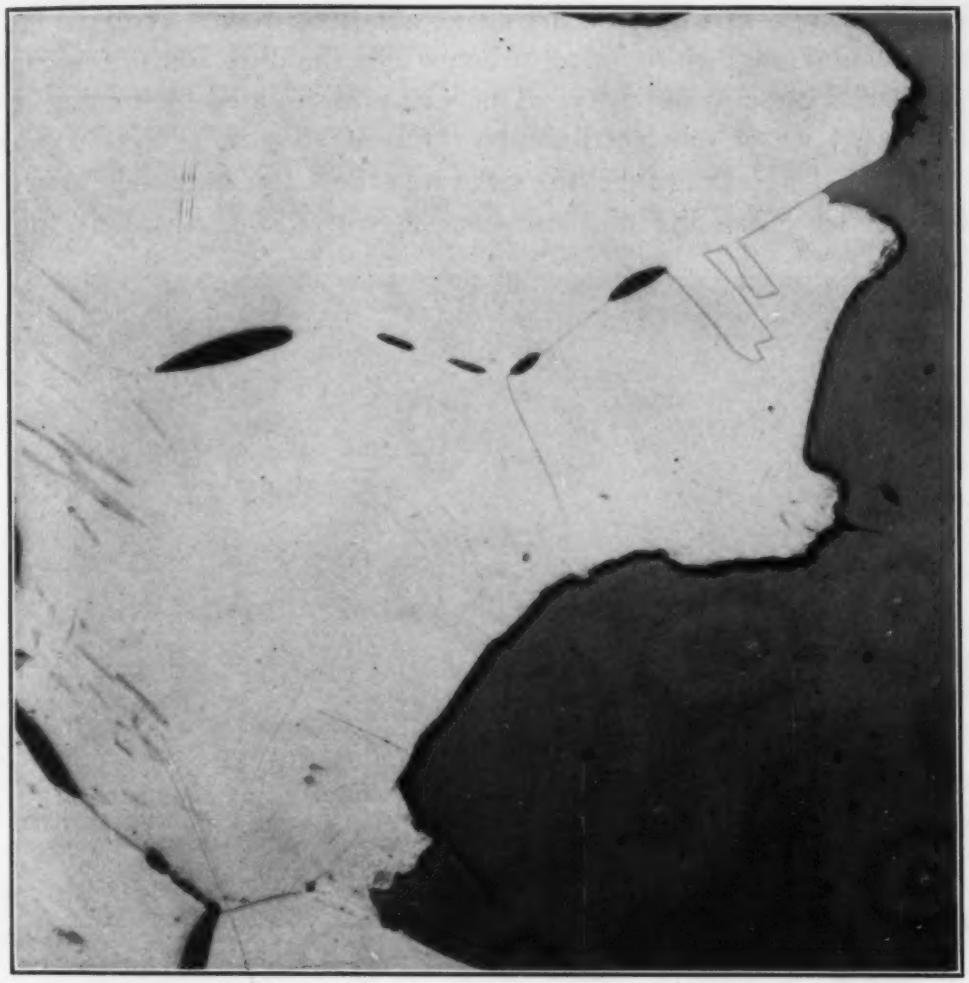

Fig. 4b—Heated 1 Hour in Hydrogen at 850 Degrees Cent., Water-Quenched. Tested in Air at 200 Degrees Cent. Stress 10,000 Pounds Per Square Inch; Life 36.6 Hours; Elongation 12 Per Cent; Reduction of Area 13 Per Cent. × 75.

quenched bars of oxygen-free high conductivity copper. The great difference in ductility is apparent in these photomicrographs.

This copper apparently contains some impurity which greatly affects the strength of the grain boundary material. The spectrographic analysis of this material shows traces of calcium, iron, silicon, and silver with low aluminum; so the element causing this tremendous sensitivity to cooling rate cannot be positively identified from these data. The rupture curve for the water quenched material indicates that this material is unstable and undergoes physical and metallurgical changes during the test. The change in slope of the rupture curve at about 4 hours is similar to the change in slope produced in rupture tests of iron by intergranular oxidation of the iron (3). The

second change in slope, occurring at about 65 hours, is apparently due to the strengthening effect produced by the diffusion to the grain boundaries of some impurity. This was substantiated by holding two unstressed water quenched samples for 400 hours at 200 degrees Cent. and then testing them the same way the water quenched samples were tested. The life of these bars (see Fig. 3) was many times

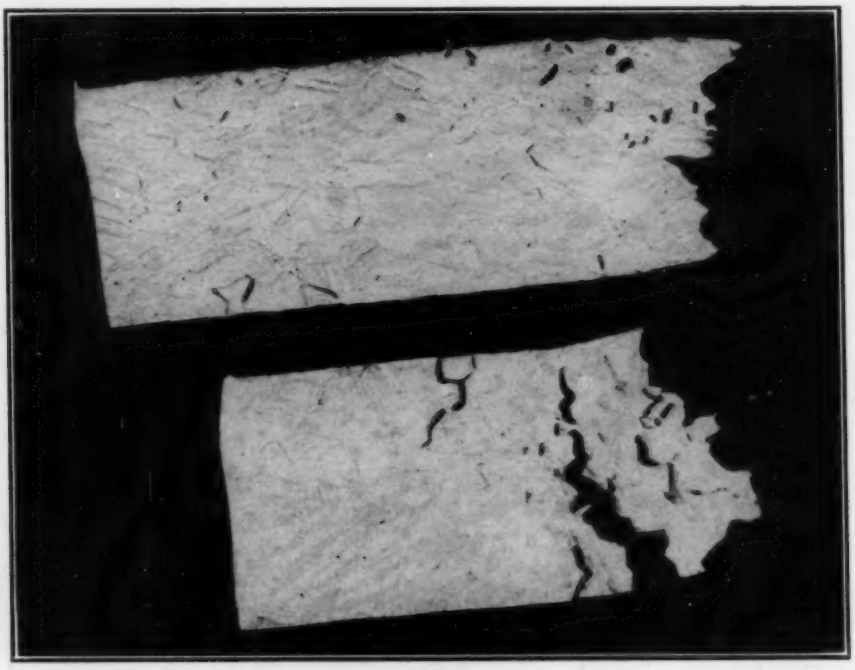

Fig. 5—(Upper) Same as Fig. 4a. × 7.2.
(Lower) Same as Fig. 4b. × 7.2.

the life of the water quenched bars with the same loads. Apparently if the water quenched material were held for a long enough time at 200 degrees Cent. it would reach a condition similar to that of the furnace cooled material.

There is some question concerning the effect of quenching strains introduced during the water quench. Quenching strains are difficult to detect in bars of this size, and even more difficult to evaluate. The bars were not warped or bent in any way by the heat treatment. To determine the effect of strain on the life under stress at elevated temperatures, some bars were bent slightly and straightened. These bars crept faster and lasted longer than the unstrained bars, just the reverse of the results produced by water quenching. Some oxygen-free high conductivity bars were air cooled to eliminate quenching strains and to further study the effect of cooling

rate on the high temperature properties. The lives of the air cooled bars were essentially the same as those of the furnace cooled samples (Fig. 3), but the air-cooled bars were much more susceptible to intercrystalline failure.

Some work was done on the recrystallization temperature of the two oxygen-free coppers and on tough pitch copper. All samples were cold-rolled from 1 inch thickness of 0.1 inch in 20 mil draughts. Before rolling, the samples were given the following treatments: The oxygen-free high conductivity copper was heated in hydrogen for 1 hour at 850 degrees Cent. and air-cooled. Two oxygen-free samples, containing silver, were heated in hydrogen for 1 hour at 850 degrees Cent. One was furnace cooled at 90 degrees Cent. per hour; the other was water-quenched. One sample of commercial tough pitch copper was rolled as received, because it had previously been annealed. Another sample of tough pitch copper was heated 4 hours in hydrogen at 1000 degrees Cent. (1830 degrees Fahr.) to remove the oxygen. The object of this treatment was to determine what effect the oxide particles had on the recrystallization of the metal.

That tough pitch copper will recrystallize at a lower temperature than oxygen-free copper has been known for a long time (1), (2), but the reason for this has been obscure. The author had previously made some experiments on the recrystallization of cold-rolled high purity iron sintered from powders. When 0.5 per cent of finely dispersed thoria was mixed with the iron powder before sintering, the recrystallization temperature of the iron was lowered at least 25 degrees Cent. This effect was attributed to the fact that inert particles act as stress raisers during deformation, causing the surrounding metal to deform more than it would if the particles were absent. It seems reasonable that the more highly deformed metal surrounding the oxide should recrystallize at a lower temperature than the metal of the sample containing no oxide. Perhaps the lower recrystallization temperature of tough pitch copper could be accounted for in the same way. To check this, a sample of tough pitch copper was deoxidized by heating in hydrogen for 4 hours at 1000 degrees Cent. (1830 degrees Fahr.) before cold rolling. Fig. 6 shows the room temperature hardness obtained after heating the rolled coppers 20 hours at successively higher temperatures. The recrystallization temperature of the sample deoxidized in hydrogen is about 25 degrees Cent. higher than that of tough pitch copper.

The oxygen-free copper containing silver showed definite precipitation hardening between 100 and 200 degrees Cent. in both the furnace-cooled and water-quenched conditions, but the hardening was more pronounced in the quenched sample, and the recrystallization was slower. It has been shown (4), (5) that the presence of

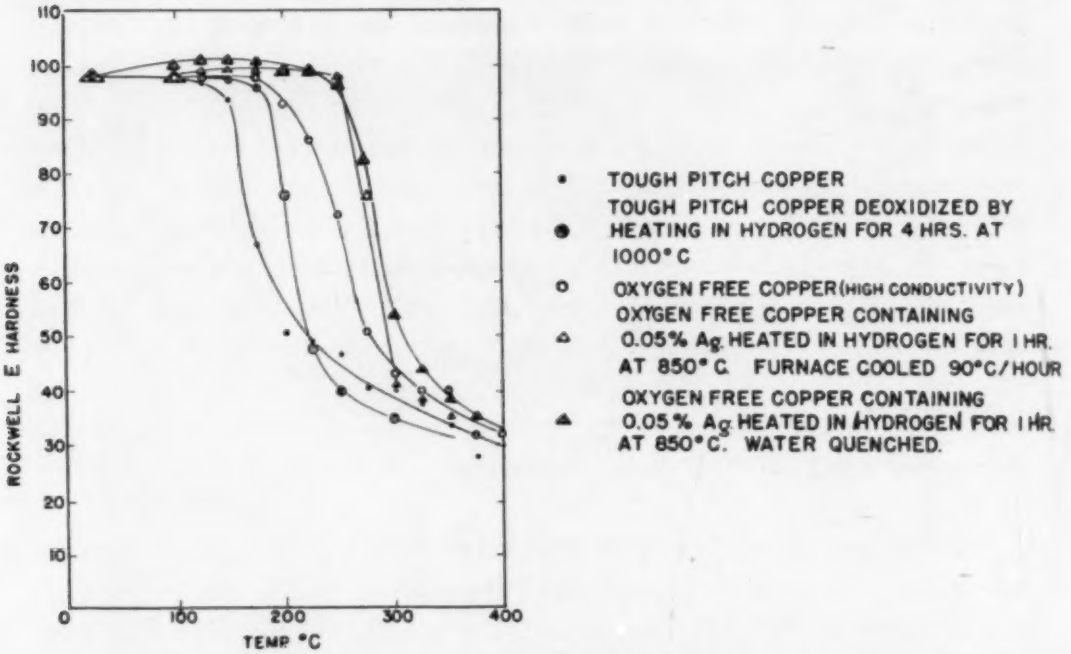
ROCKWELL E HARDNESS
TEMP °C
TOUGH PITCH COPPER
TOUGH PITCH COPPER DEOXIDIZED BY HEATING IN HYDROGEN FOR 4 HRS. AT 1000° C
OXYGEN FREE COPPER (HIGH CONDUCTIVITY)
OXYGEN FREE COPPER CONTAINING 0.05% Ag. HEATED IN HYDROGEN FOR 1 HR. AT 850° C. FURNACE COOLED 90°C/HOUR
OXYGEN FREE COPPER CONTAINING 0.05% Ag HEATED IN HYDROGEN FOR 1 HR. AT 850° C. WATER QUENCHED.

Fig. 6—Recrystallization of Copper Samples Cold-Rolled from 1 Inch to 0.1 Inch. Hardness Measured after 20 Hour Reheats at Successively Higher Temperatures.

a finely dispersed precipitate of a metallic phase will cause a marked rise in recrystallization temperature. The precipitation which occurs in the cold-rolled copper containing silver may be responsible for the high recrystallization temperature of this material.

That particles of a dispersed phase may lower the recrystallization temperature of a metal in one instance and raise it in another may seem contradictory. However, it seems likely that the particles may affect the metal in several ways and that certain effects may predominate for certain sizes and distributions of the particles. The following suggestions are offered in explanation of the difference observed between the effect of the oxide particles and the effect of the finely dispersed metallic phase. The hard oxide particles cause considerable extra strain in the surrounding metal during deformation. The relatively ductile solid solution precipitate was probably not present in an appreciable quantity during deformation (precipi-

tation hardening occurred when the cold-rolled copper was heated), and so could not add much to the average strain. A dispersed phase in a cold-worked metal disturbs the continuity of the metal lattice and presumably interferes with the formation of an unstrained lattice. Large particles a considerable distance apart would contribute extra strain but offer little interference to the motion of copper atoms during recrystallization. A fine uniformly distributed precipitate such as that present in the copper containing silver offers a maximum interference to recrystallization.

The foregoing considerations are offered as an explanation of the observed behaviors. The possibility that the nature of the particle, i.e., metallic or nonmetallic, may be important should not be overlooked, but at present this consideration seems secondary in importance.

Conclusions

1. It is suggested that in copper containing a small amount of silver, the silver tends to concentrate in the grain boundary material. The higher concentration of silver in the grain boundaries results in a strengthening so that a higher temperature is necessary to produce an intercrystalline fracture in a given length of time.

2. Small quantities of other elements in copper can produce effects similar to those produced by a small quantity of silver in copper; e.g., the stress required to fracture oxygen-free high conductivity copper in 100 hours at 200 degrees Cent. (390 degrees Fahr.) can be varied 40 per cent by a difference in cooling rate from 850 degrees Cent. (1560 degrees Fahr.).

3. Oxidation is known to affect the high temperature strength of steels (3), but the role oxygen plays in the high temperature strength of copper remains to be determined.

4. The low recrystallization temperature of tough pitch copper is at least partly attributable to the presence of the oxide particles. These particles apparently act as stress raisers and cause more than average strain in the surrounding metal during cold working.

5. Cold-rolled oxygen-free copper containing 0.054 per cent silver was found to slightly but definitely precipitation harden when heated between 100 and 200 degrees Cent.

6. It is suggested that the precipitation which occurs in the cold-rolled copper containing silver is responsible for the high recrystallization temperature.

ACKNOWLEDGMENTS

The author is indebted to T. S. Fuller and S. Rolle for the oxygen-free copper, containing silver; to L. E. Osman for assistance in conducting the experiments; and to L. L. Wyman and Mrs. C. B. Brodie for the photomicrographs.

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DISCUSSION

Written Discussion: By F. N. Rhines, assistant professor, department of metallurgy, Carnegie Institute of Technology, Pittsburgh.

At the risk of being accused of "seeing portraits in rocks", I venture to suggest that the structures shown in Figs. 4a and 4b look very much like those usually associated with the hydrogen embrittlement of copper. Indeed, the differences in the outlines of the cracks or holes at the grain boundaries in these two samples (if the dark areas do, in fact, represent holes) are of the type to be expected in the event of hydrogen embrittlement followed by a quench in the one case and a prolonged anneal in the other. C. S. Smith and C. R. Hayward (*Journal,* Institute of Metals, Vol. 36, 1926, p. 211) in their study of the hydrogen embrittlement of cast copper found that during the early stages of embrittlement, extensive cracks occurred at the grain boundaries, and that with the passage of time at an elevated temperature these closed and welded to a limited extent, leaving occasional holes instead of long cracks and restoring the ductility of the metal to a considerable degree. In Fig. 4b elongated dark areas appear along the grain boundaries, whereas in Fig. 4a the corresponding areas seem to be much shorter and rounded. Since the sample represented in Fig. 4a was subjected to a much longer heat treatment as a result of its slow cool, does it not seem possible that cracks already present as a result of hydrogen embrittlement and preserved by quenching

the sample of Fig. 4b have been partially closed in the sample of Fig. 4a? If so, the differences in the mechanical behavior of the quenched and slowly cooled samples might now be explained by the presence in the quenched metal of longer cracks than are found in the slowly cooled sample, leading to earlier failure and a more obviously intercrystalline fracture.

The use of "oxygen-free" copper in these experiments does not necessarily preclude hydrogen embrittlement. In the Metals Research Laboratory, we have recently been able to show that oxygen-free copper can absorb enough oxygen during an oxidizing anneal to make it mildly susceptible to hydrogen embrittlement thereafter. In the absence of a detailed description of the fabricating technique used in making the samples it is difficult to judge whether or not there was opportunity for the absorption of oxygen, but a very special procedure would have been required to prevent it.

It is not my purpose to cast doubt upon the validity of the observations or conclusions of this very interesting paper, but rather to point out that the meaning of the results would be clarified by establishing the absence of hydrogen embrittlement. Perhaps the substitution of a dry CO atmosphere or a vacuum for the hydrogen in the annealing treatment would provide a practical means of accomplishing this object.

Written Discussion: By Sidney Rolle, The Scomet Engineering Co., New York.

Mr. H. M. Schleicher, our metallurgist, and I have read Mr. Parker's paper with a great deal of interest, not only because we furnished the OFHC and the OFHC containing silver used in the investigation, but because he has brought to light properties of these metals about which we are as yet not very well informed. He has done a nice piece of work for which he deserves high praise. However, it is regrettable that he was not suspicious of the spectrographic analyses, particularly as he was endeavoring to determine what the effect of the impurities has on the properties of the metals at high temperature.

Mr. Parker, it is true, calls the analyses "qualitative", but even so, our many years of experience in producing OFHC forces us to question the correctness of these figures. We should be very much pleased with ourselves if we could say that we were producing copper commercially of this quality; but alas, we have not yet reached that goal, despite much effort in the tank house to improve the already high quality of the cathodes and in the casting department where these cathodes are melted under very careful control of atmosphere and temperature. All of this has made us acutely aware of the effects of the impurities.

We believe that Mr. Parker was at a disadvantage in not having the proper quantitative analysis of the metals he used, which by the way were commercial products and not specially prepared.

It might be well to cite here the analysis made on a sample of OFHC copper used by Mr. Schleicher and myself in studying the effect of impurities on the annealing and drawing characteristics of various kinds of oxygen-free copper. The results of this investigation were published in an article which appeared in the March, 1940, issue of *Metals and Alloys*. The analysis of the OFHC copper is given in the table on the following page.

Element	Per Cent Impurity	Method of Analysis
Silver	0.0022	Chemical
Aluminum	N.D.	—
Arsenic	0.0004	Chemical
Boron	N.D.	—
Barium	N.D.	—
Bismuth	Trace	Spectrographic
Calcium	N.D.	—
Iron	0.0016	Chemical
Iron	0.002	Spectrographic
Manganese	0.0005	Spectrographic
Nickel	0.0005	Spectrographic
Nickel	0.0007	Chemical
Lead	0.0007	Chemical
Lead	0.0005	Spectrographic
Antimony	0.0006	Chemical
Silicon	0.0004	Chemical
Silicon	0.0010	Spectrographic
Tin	0.0001	Spectrographic
Sulphur	0.0040	Chemical
Selenium	0.0003	Chemical
Tellurium	0.0012	Chemical

The foregoing shows that the analysis reported by Mr. Parker of the OFHC we furnished him, does not check with our analysis of the same kind of material. The total of 13 impurities reported by us is about 0.013 per cent and if we add to this the traces of aluminum and calcium, reported by Mr. Parker, the total is even higher. We are, however, under the impression that these latter elements are from the electrode used in the spectrographic analysis.

Any one of the elements by itself in the amount present would probably have little or no effect on any of the physical properties of the copper, but collectively they undoubtedly do have an effect and their presence must not be ignored either in production or in research.

As is well known, most of the impurities found in the castings are carried over from the cathodes but the fact that certain properties, such as the electrical conductivity, when determined on wire made directly from cathodes, is about a per cent higher than when determined on wire made from OFHC castings, leads to the conclusion that many of the impurities which are entrapped in the cathode are dissolved in the melted copper and are in solid solution. Chemists have found that when making oxygen determinations on copper, using the well-known hydrogen method, the container used for holding the copper invariably shows a sort of metallic ring near the exit end which is due to the volatilization of some of the impurities.

Among the elements which tend to come out of OFHC copper during the hydrogen treatment are sulphur, selenium, tellurium, bismuth, arsenic and antimony. Since a gaseous product is made by the reactions, some internal pressure may develop and an action analogous to the embrittling due to oxygen elimination, takes place; but only to a very slight extent. From this it is logical to expect that certain properties of the metal before being annealed in hydrogen will differ from those of the same metal after annealing. In our opinion, this fact is of great importance, and inasmuch as the abstract of this paper contains no reference to hydrogen annealing, the statements made appear to be rather broad.

A study of the photomicrographs in Mr. Parker's paper leads us to believe

that the open boundaries shown are not primarily due to hydrogen embrittlement, even of the kind just mentioned. We have looked at many sections of OFHC copper after hydrogen treatment and have never come across anything like the condition shown in these photomicrographs.

However, a somewhat similar condition has been noted in OFHC copper which had been cold-worked in the cast condition. Although the copper is soft, the gradual reduction usual in cold-working does not "work" the whole structure sufficiently, and strong differential stresses are set up in the interior of the casting which cause rupture. All of the material we furnished Mr. Parker was cast copper, and it is not made clear in the paper how it was reduced and we should like to ask him if the material was directly cold-rolled, that is, without intermediate hot rolling.

Coming back to the question of the annealing or softening temperatures, in the article* cited earlier in this discussion, reference is made to the investigation conducted by Webster, Christie and Pratt,** who found that 0.022 per cent of silver in Lake Copper, high in arsenic and antimony and containing

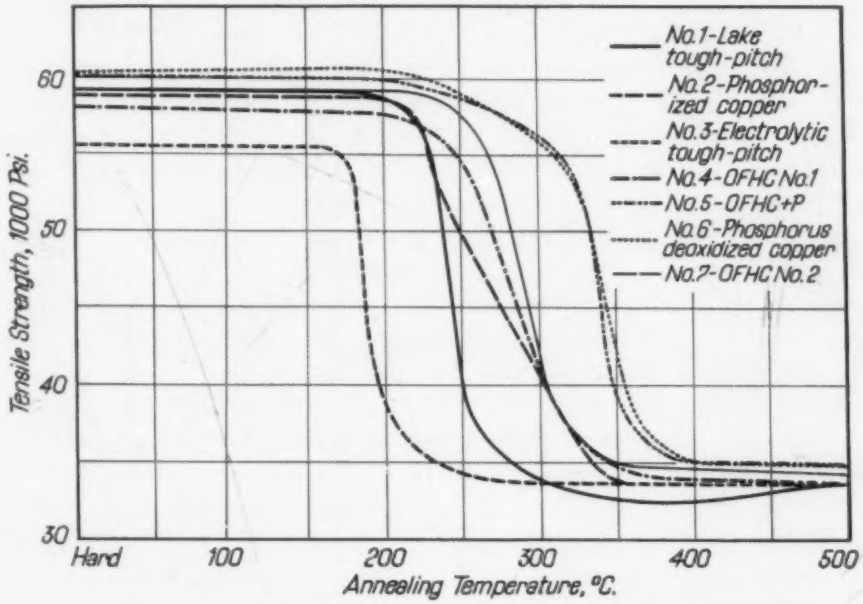

Fig. A—Tensile Strength Curves of Six Types of Copper.

normal amount of oxygen—0.033 per cent—did not raise the softening temperature as much as 0.013 per cent of miscellaneous impurities in OFHC copper.

The annealing characteristics of OFHC copper, tough-pitch Lake Copper and four other kinds of copper were shown in Fig. 8 of the article by Mr. Schleicher and myself. This is reproduced in Fig. A.

The curves shown indicate that softening, as measured by reduction in the tensile strength, develops in tough-pitch copper at about 225 degrees Cent., whereas with OFHC, softening does not take place until a temperature of

**Metals and Alloys,* March, 1940.

***Proceedings,* Institute of Metals Division, American Institute of Mining and Metallurgical Engineers, 1927 and 1933.

about 350 degrees Cent. is reached. In tough-pitch, containing say 0.035 per cent oxygen, equivalent to about 0.315 per cent cuprous oxide, nearly all the impurities are oxidized and are located in the grain boundaries. In OFHC copper, which is free from cuprous oxide, nearly all the impurities remain in solid solution.

Author's Reply

I wish to thank Mr. Rolle and Dr. Rhines for their contributions to this paper. I am sorry that our spectrographic analysis was not quantitative, but we are not equipped to make analyses of this type. The analyses presented by Mr. Rolle adds materially to the value of the paper. The variations in strength of the OFHC copper reported in the paper, as suggested by Mr. Rolle, probably result from the collective effects of many impurities. Mr. Rolle asked how the cast copper which he furnished was reduced. The cast copper was first reduced hot in the manner recommended for OFHC copper. The cold working referred to in the paper was done only on bars which had been previously reduced hot.

Dr. Rhines is suspicious of the open grain boundaries and suggests that they may be the result of some form of hydrogen embrittlement. The following precautions had been taken and experiments performed to demonstrate that hydrogen embrittlement was not the cause of the effects described in the text. A large quantity of material was machined from the surface of all hot reduced bars to remove the oxidized layer which had formed during the working. Also, a considerable quantity of material was cut from the surface of the cold-worked bars during the machining of the test bars. As an additional precaution, some bars were sectioned and examined microscopically; no oxide could be found in any of the bars examined. Some bars were also sectioned and examined microscopically for embrittlement after the hydrogen treatment; no evidence of embrittlement could be found. Other bars were broken in tension at room temperature, and these bars were also examined microscopically. The tensile loading would have exaggerated the condition of open boundaries had any embrittlement taken place; no open grain boundaries were found in these bars. In addition to the tests on hydrogen-annealed samples, bars which had been heat treated in air and in vacuum (approximately 10^{-6} millimeters of mercury) were also tested. These bars had never been in a hydrogen atmosphere, yet the same effect (quenched bars much weaker in rupture tests) was found with these bars as with the hydrogen annealed bars. However, the magnitude of the effect differed slightly for each treatment, hydrogen, air, and vacuum, because of the slightly different cooling rates during the quench from the three treatments. The samples treated in air were 0.5-inch diameter bars from which the test samples were machined. The test samples treated in vacuum were sealed in evacuated quartz tubes. Some samples were furnace cooled in vacuum; other samples were water quenched by breaking the end off the quartz tube and dropping the samples into water. In view of these tests, it seemed that hydrogen embrittlement could not be the cause of the effects observed.